AMULLAN PHAMILAN AND AROMATICS



OCTOBER 1958

THE MAGAZINE OF TASTE AND SCENT

12 Top
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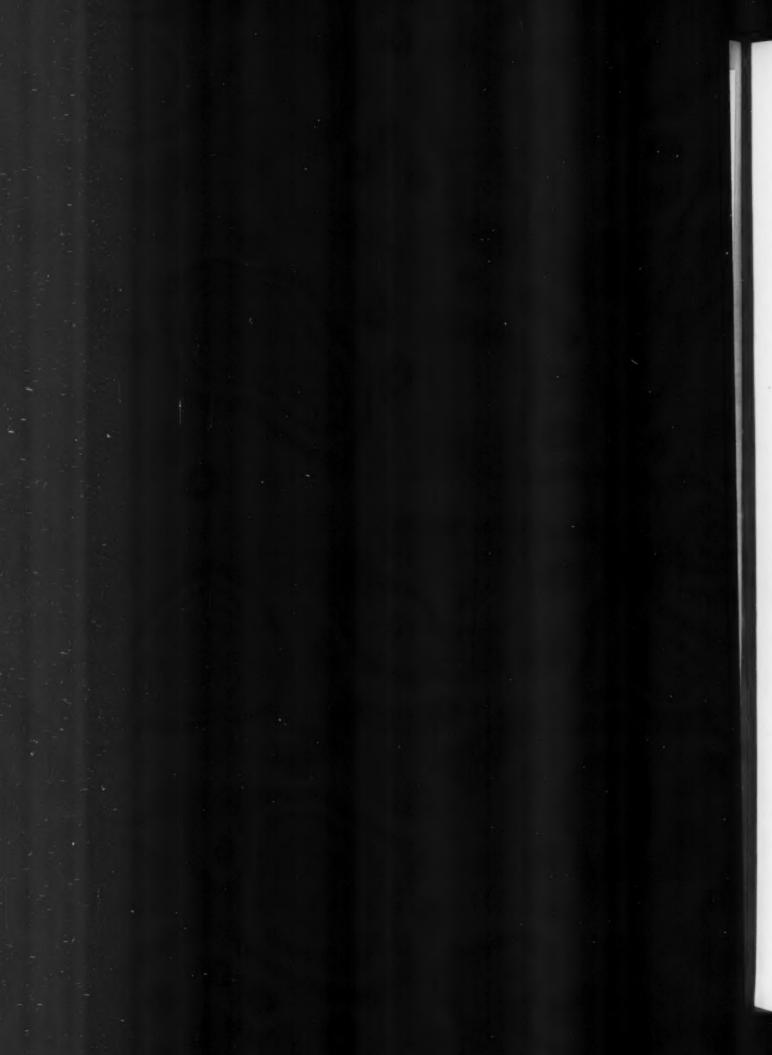


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AND AROMATICS

VOL. 72, NO. 4

The Commercial Surfactants

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Things are not always what at first they seem. In Maine, a souvenir replica of a lobster trap had "Made in Japan" rubber stamped on the under side.

I am not against rubber stamps, as such. They have their use in commerce. When PAID is stamped on an invoice, it shows that a financial obligation has been met. In the publishing business, there is a highly esteemed, more emphatic way of saying PAID.

It is

But its use is restricted. That right has to be earned; not once, but over and over again. In other words, a publication must qualify on a continuing basis to be able to display and use this meaningful insignia.

Let's see what (181) really means.



It means that a publication is being sent to someone who thinks highly enough of its value to want to have it reach him regularly and who makes that crystal clear by going to the trouble and expense of paying for it.

It means that there has to be enough of these someones to form an audience in a clearly defined market that can be and is subjected to identification and classifica-

It means that this clarification of type of reader and translation into a market rests not alone with the publication, but is subject to verification by periodic audit by independent specialists in evaluating circulation and method.

It must also mean, if I have made myself It must also mean, if I have made myself clear up to this point, that there obviously exists a governing body with authority (1) to grant the right of use of the ABC insignia, (2) to protect and to monitor its integrity and all that it stands for, and (3) if given just cause, to withdraw the privileged use of this great denominator of paid circulation and markets. circulation and markets.

Such is the case; in full name it is known as the Audit Bureau of Circulations. Its initials form the time honored and universally accepted insignia of qualitative circulation—market measurement.

The members of the Audit Bureau of Cir-The members of the Audit Bureau of Circulations are publishers, advertisers and advertising agencies. Although the publisher members pay 90% of the total expense, they give the majority voice to advertising buyers.

The American Perfumer and Aromatics is indeed proud of its twenty-two years of authenticated membership in the Audit Bureau of Circulations.

But remember ABC is the best assurance a subscriber has that the publication is edited first for his interest and is the best assurance an advertiser has that the publication is paid for and wanted by its subscribers

James H. Moore, Jr. Publisher

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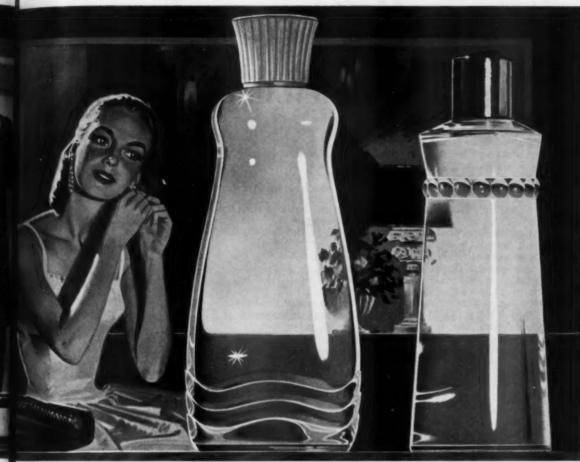


Merchandising Cartons

Modern cartons are developed only through systematic consideration of their opportunity to serve you in the retail store and warehouse... as well as on your own filling line and in transit.







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HESPERIDOL H5... the tantalizing aroma of freshly peeled oranges.

LATYRON-A... the fresh, invigorating note of new-mown hay.



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ROSE HV: Compounded rose base processed by extraction in presence of flowers other than Rose de Mai.

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You are invited to send for samples of any specialties that interest you.

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Food Additives Must be Proved to be Harmless

Manufacturers must prove that food additives are harmless in their intended use if they do not already fall into the exempt or safe classes or they will have to remove them from the market since President Eisenhower signed the food additive bill into law September 6. Under the schedule of deadlines producers of additives that were in use prior to this year have 18 months in which to prove that their materials are harmless. Manufacturers of additives that were introduced this year have six months to comply. Proof must be given to the Food & Drug Administration as to the harmlessness of additives.

Warner-Lambert to Merge with Reynolds Tobacco Co.

Warner-Lambert Pharmaceutical Co., one of the oldest and largest cosmetic and pharmaceutical concerns in this country is to be merged with the R. J. Reynolds Tobacco Co., Winston-Salem, N. C. January 1, 1959. Combined sales of the two big companies are over \$1,206,000,000; and both companies are regarded as being depression proof. The merger is reported to be on a one-for-one share of stock basis with the probability of a three-for-one split later. New Class B Reynolds stock is to be the basis for the exchange it is reported. The R. J. Reynolds Tobacco Co. is one of the three largest companies in its field. It manufactures Camel, Winston, Salem and Cavalier cigarettes; Carter Hall, George Washington and Prince Albert smoking tobacco; Day's Work and Brown's Mule chewing tobacco and sundry tobacco products. Warner-Lambert Pharmaceutical Co., Morris Plains, N. J. is one of the oldest and largest companies in the pharmaceutical and cosmetic industries. Warner-Chilcot Laboratories a division, manufactures ethical pharmaceuticals and physicians' specialties exclusively for the medical profession and drug trade. Standard Laboratories, a division, manufactures Sloan's liniment and balm, Vince and Hobsons proprietary medicines, Nospi, Stacomb and Bathasweet. Nepara Laboratories is a division. In the Family Products Division are included Anahist products, Bromo-Seltzer and Fizzies, Listerine products, Richard Hudnut toiletries, Rimmel, Inc., perfumes and mascara and Ciro Inc. perfumes. The latter two are French concerns. Also included are DuBarry products, Sportsman men's toiletries and the Florence Manufacturing Co. tooth brushes. As both companies are in the consumer products field it is felt that the merger is of advantage to each. Warner-Lambert's position should be improved by securing prime television and radio advertising spots in the highly competitive field and Warner-Lambert's foreign operations would be useful in selling Reynolds products abroad.

Parfums Evyan Goes Into **Motion Picture Business**

Parfums Evyan, Inc., New York, founded by Evelyn Westall, its president, which has met marked success with its perfumes White Shoulders, Most Precious, Golden Shadows, Gay Diversion and Enchanting Menace, is going into the motion picture business. A new company, Evyan Productions has been organized with a Delaware charter which plans to produce "King William, the Conqueror". The new company has purchased rights to the novel by R. B. D. Wilson Evans on which the movie will be based; and has engaged Aeneas Mackenzie to write the movie script from it. It is to be filmed in England and in Hollywood under the direction of Royben Mamoulian, A. E. Hamilton, a vice president of the new company who was formerly with Desilu Productions will be the producer and Dr. and Mrs. Walter Langer will be executive producers. In private life Evelyn Diane Westall is Mrs. Walter Langer, wife of Dr. Walter Langer, the brilliant chemist. Mrs. Langer is the former Lady Clinton Westall. Dr. Langer was Baron von Langendorff of Austria, before becoming a United States citizen. Evelyn Westall Langer is president and Dr. Walter Langer is vice president of the new motion picture company.

Helena Rubinstein Signs Pact With Union for Dental Care Probably the first non-profit dental insurance plan to be negotiated between labor and management was signed by Helena Rubinstein Inc. and Local 14-149 of the Oil, Chemical & Atomic Workers Union A.F.L. and C.I.O. The plan is to be administered by Group Health Dental Insurance Inc. of New York. Helena Rubinstein will pay the monthly premium of \$1.65 and employes can employ their own dentists.

Vick Sells Cosmetic Lines to Chesebrough-Pond's Chesebrough-Pond's Inc. has purchased for an undisclosed amount of cash the cosmetic lines of Vick Chemical Co. These include Prince Matchabelli and Simonette perfumes and cosmetics; Seaforth and Black Watch men's toiletries and Sofskin hand creams. The Prince Matchabelli line will be sold as in the past through approximately 5,000 class outlets; Sofskin hand creams will be added to Chesebrough-Pond's line; and the Seaforth men's toiletries will join the Vaseline brand products. Vick disposed of the cosmetic lines because over 90% of its business was concentrated in the drug and closely related fields. Vick will invest the proceeds of the sale in its acquisition program. In the past few months it acquired Walker Laboratories and the Lavoris Co. The purchase of the Vick cosmetic lines will give to Chesebrough-Ponds a more diversified volume and a stronger potential in the retail field. J. A. Straka, president of Chesebrough-Pond's and H. S. Richardson Jr. president of Vick Chemical Co. described the purchase as a mutually beneficial sale.

Cosmetic Manufacturers
Using More TV Film Shows

The number of cosmetic and drug manufacturers sponsoring syndicated film shows has increased 38% in the past two years according to a survey by Ziv Television Programs, Inc.

Government Fixes New Minimum Soap Wage Scale A minimum wage rate of \$1.50 per hour for the soap industry has been fixed by the Department of Labor, Washington, D. C. It went into effect August 15 and must be paid to employes in the industry working on government contracts in excess of \$10,000. General regulations will govern the employment of handicapped persons and apprentices at wages lower than \$1.50 per hour. The government purchases around \$10,000,000 worth of soap products annually.

Lever Bros. Purchase of "All" Basis of Anti-Merger Suit The Department of Justice of the United States has filed an action against the Lever Bros. Co. and the Monsanto Chemical Co. which may force Lever to divest itself of the detergent "All." The government claims in a civil action against the two companies that Lever got control of "All" in return for a promise to purchase Monsanto products. The anti-trust division contends that the acquisition violates the merger law of 1950 by eliminating actual and potential competition between the two companies. Previously according to the complaint Monsanto had approximately 5% of the detergent market with "All." After the acquisition Lever had 20% and no longer had to compete with Monsanto. Lever Bros. Co. is resisting the complaint and expects to win.

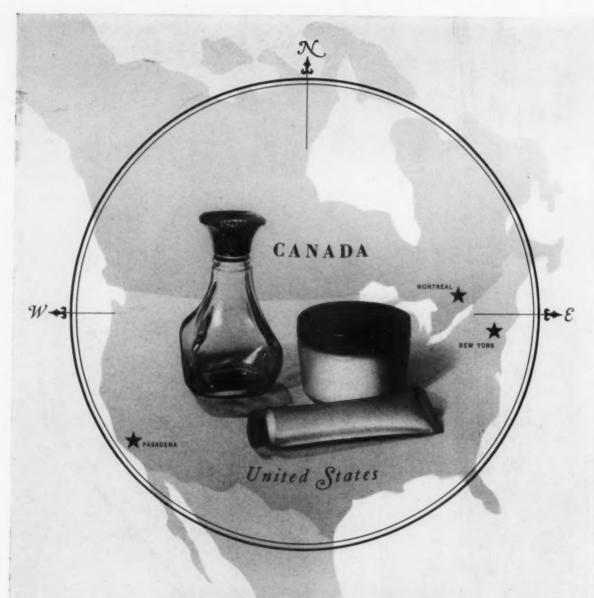
New Method for Low Cost Doorto-Door Shipping by Air Any package up to 40 lbs. may be delivered door-to-door to any town in the United States in from one to three days at rates comparable with surface transportation by Parcel Air System, a division of American Shippers Inc., 315 West 36 St., New York. The new service uses Parcel Air stamps in denominations of 5 cents, 25 cents and one dollar. The stamps are used to prepay and predetermine delivery charges so as to eliminate waybills, auditing and delays in billing. The quick pickup and delivery employing trucks, utilizes the speed of all scheduled airlines for the long runs. Means for insuring parcels are provided. The service was begun April 7 in New York, Boston, Chicago and Los Angeles and other terminal points will be opened soon. Parcel Air points out that a 20 lb. package shipped from Los Angeles by air express from Los Angeles to New York would cost with \$50 insurance coverage, \$17.08; by air freight, \$19.70; by air parcel post, \$16.20; and by Parcel Air, \$4.90. Ground transportation by rail express was quoted at \$5.42 with straight parcel post, \$3.95.

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Maison G. deNavarre, M.S., F.A.I.C.

Woolfat Sterols and Liver

A publication by Duncan and Best (J. Nutrition, 64, 425, 1958) on the effect of the addition of 2 per cent lanolin "isocholesterol" and three pure components—lanosterol, dihydrolanosterol and agnosterol—to cholesterol, in the diet of rats is thought provocative. The authors find that "isocholesterol" and its components exerts an inhibitory effect on cholesterol accumulation in the liver. Dihydrolanosterol, agnosterol "isocholesterol" and lanosterol, in that order, showed their inhibitory effect.

Suntan Pills

It is good to see the report of Sulzberger and Lerner (J. A. M. A., August 23, 1958) on the use of so-called suntan pills (8-methoxypsoralen) questioning its safety for regular use over long periods of time. While the authors report that many investigators feel that 8-MOP helps tanning, there is a fine line of demarcation between dosage and solar exposure. Some of the side effects of oral ingestion, such as liver and gastrointestinal disorders are discussed.

For the time being 8-MOP is a prescription item awaiting results of wider usage over longer periods of time.

Body Color Capsules

Peter Simple's column in the "Daily Telegraph" (London) for August 14, describes a new product for the British market, to be sold

as a capsule and taken internally. By doing so, your entire body takes on various shades. There is a creamy tint for blondes, a sultry tan for brunettes and a pallid shade for redheads. A neutralizing capsule can be taken to change from one shade to another.

The product is the brain child of an endocrinologist, says Simple. Furthermore, it lasts twenty-four hours giving a uniform coloring without streaks. (Now I hear it is all a joke. Did sound too good to be true.)

All I can say is, if it is safe and does what Simple says, it is no less than remarkable.

Soap Germicide

Another soap germicide recently made available is a N-trichloromethylthiotetrahydrophthalimide, used in a 2 per cent concentration in bar or liquid soap. It is claimed to be economical and safe.

Recently seen was a bar of soap made with trichlorocarbanilide that was fifteen months old. Looked pretty good, too. Very little effect on odor.

Of course, there is hexachlorophene, bithional and P.C.M.X., all useful in about a 2 per cent concentration.

Silicon in Skin and Hair

Fregert publishes one of the few reports on the silicon content of skin, hair and nails among others, in the J. Invest. Dermatol., 31, 95, 1958.

It is interesting to note that on

a dry basis, epidermis contains 106 gamma/gm., hair 90, nails 56, male dermis with strong hair growth 25, and male dermis with weak hair growth 19 gamma with a plus or minus factor specific for each.

Ichthyotic skin contained more silicon than skin with psoriasis or exfolicative dermatitis. All analyses were made by the recently published method (1955) of King et al.

White Silica Powder

A new white, finely powdered (av. 16 millimicron particle size) silicon dioxide, 97-98 per cent pure with 0.04 per cent iron, manganese and copper 0.0001 per cent each weighing 9½ to 10½ ounces per gallon is now available. Water suspension (10 per cent) has a pH of 6.0; refractive index is 1.55.

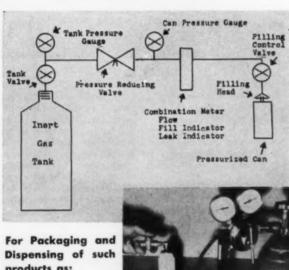
This is a versatile inert carrier for fragrance in sachets, powders, bath salts and other loose dry products. Its high specific gravity (1.9-2.0) would be against it in suspensions as a perfume carrier, but it could serve as a low covering power pigment.

Notes

Bob Holland, who looks very well by the way, gave me an interesting run-down on Aloe Vera in cosmetics, a project underway in Florida, where he has spent a little time lately.... It's an interesting hassle between the dentifrice ad claims, the Blatnik Committee and the A. D. A. . . . If "they" have to take out claims or implications of fabulous results from the use of Royal

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Jelly or placenta substance, what can "they" say to justify the price? . . . French Patent No. 1,130,934 covers the use of beer (Pilsner, lager, Bock or what?) with triethanolamine lauryl sulfate and a glycol alginate thickener as a shampoo for human hair-it is supposed to help wave hair. . . . Abstracts of about 140 Russian scientific journals are available in English from the Office of Technical Services. U. S. Department of Commerce. Washington 25, D. C., at various fees, depending on the journal abstracted. . . .

Surfactant Notes

The Tariff Commission reports that year was a good one for surface active agents. The total output was 1.206.000,000 lbs .- an increase of 5% over the previous year. These statistics given in its preliminary report on the production and sales of surface active agents are about 95% complete. The complete statistics will be given in the final report on the production and sales of synthetic organic chemicals to be issued later this year.

Sarkosyl, N-acyl sarcosine surfactants are covered in a technical bulletin issued by Geigy Industrial Chemicals division of the Geigy Chemical Corp., Saw Mill River road Ardsley, N. Y. The bulletin contains 16 pages and describes the surfactants giving chemical and physical properties, uses as corrosion inhibitors, physiological properties and analytical methods. Uses in cosmetics such as dentifrices, shampoos, detergents etc. are also given.

Non-ionic surface active agents which are insensitive to hard water and electrolytes prepared from glycerine and propylene oxide are covered in U. S. Patent 2,831,034.

A 40-page technical bulletin on Surfonic surface active agents which find extensive use in cleaning compounds is available from the Jefferson Chemical Co., 1121 Walker Ave., Houston, 2, Texas.

Reprints of the revised "Surfactant Listing" including trade names, manufacturers, classifications, formula data and end uses for over 2,000 surface active agents are available at \$2.50 from John W. McCutcheon Inc., 475 Fifth Ave., New York, 17, N. Y.







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"MEXICO O F., AND BUENOS AIRES ARGENTINA FACTORIES.
CLIFTON N J. AND BUENOS AIRES ARGENTINA.





... Dainty, appealing lily of the valley ...

Dewy fresh, demurely sweet and

everlastingly lovely.

... A lively blend of florals...The perfect accompaniment for an exuberant, gay, youthful personality.

.. Truly, a most beautiful fragrance...
A lilac blend... Tender, warm
and extremely wearable.

A Fragrant Foursome of Captivating Perfumes for Milady's Growing Daughters . . .

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BY FRITZSCHE



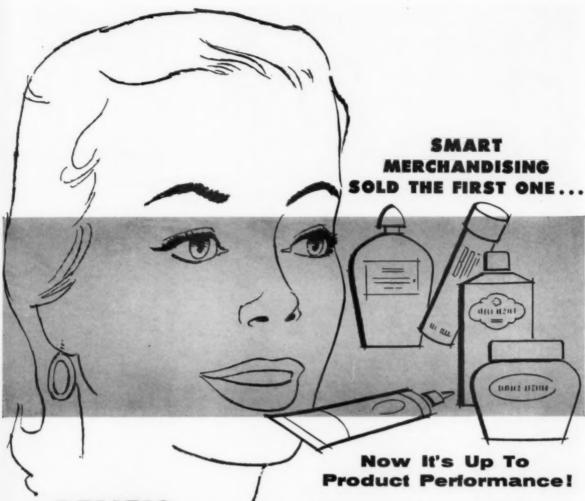
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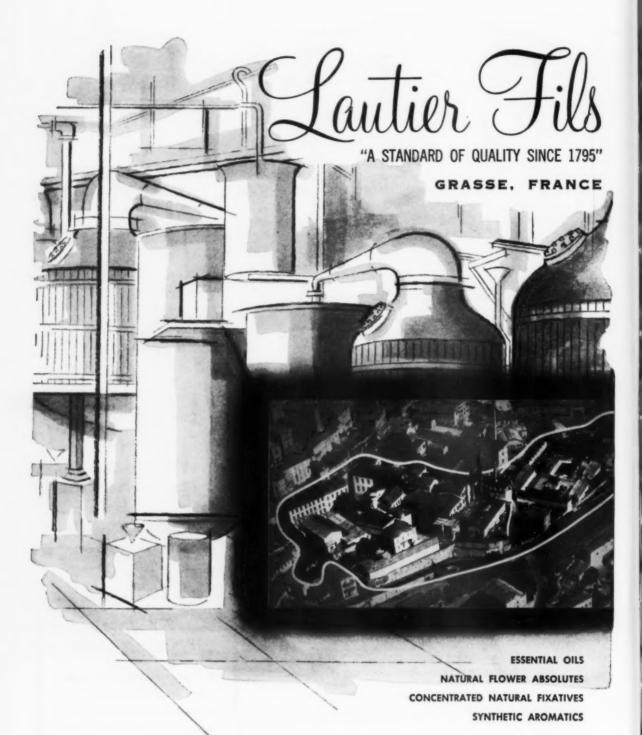
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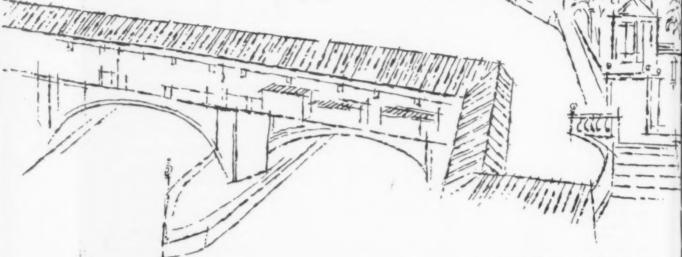
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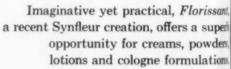
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PRODUCTS & IDEAS

OPTICAL GONIOMETER-1

A new optical goniometer manufactured by Arthur S. LaPine and Co. enables chemists to identify crystalline substances by simple external measurements of interfacial angles. Recent publication in England of the Barker Index of Crystals has aroused widespread interest in the potential of a simple method of optical analysis of substances that crystallize.

The Techne two-circle goniometer measures angles between the faces of tiny crystals by catching reflections from the various faces in a telescope which is moved on a graduated scale around the crystal. The goniometer is reported to be accurate within 3 minutes of arc and extremely simple to operate

SUBMICRON FILTER

per

lers

and

ons nity est, The Barnstead Still and Sterilizer Co. announces a new submicron filter Model MF-25 for use in laboratory work, pharmaceutical manufacturing, and wherever an exceptionally pure water supply is desired. The unit is for use primarily with distilled or demineralized water where it removes particulate matter down to 0.45 micron, according to the manufacturer.

The filter media is the Millipore cellulose ester membrane. Standard units are constructed of bronze lined with pure block tin on the interior surfaces. It can also be supplied with Teflon or Kel-F interior coating for special applications. In addition, inner surfaces may be nickel coated or the entire unit may be made of stainless steel or aluminum if desired.

Special features of this unit include long legs to permit placing containers underneath and to facilitate inlet and overflow hose connections to the special stainless steel nipples. Total height is 20 inches. Rate of flow is 25 to 100 gallons per hour.

LABORATORY BALANCE-2

Henry Troemner, Inc. offers the new Troemner/400 series of balances designed to further simplify and speed determinations requiring sensitivity as close as 2 mg. A new, easily-read single pointer and a wider graduated beam are clearly visible for weighing with the lid closed. There is said to be ample room between the stainless-steel

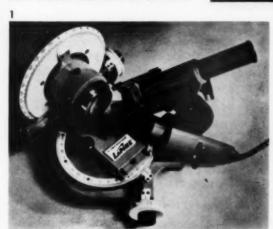


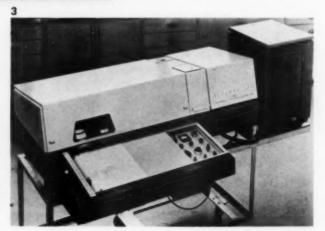
pans and the lid for weighing at full capacity with the lid closed. The metal case is finished in chemicalresistant gray baked enamel and chrome. A new universal leveling bubble and larger chrome screw-feet are offered as additional improvements.

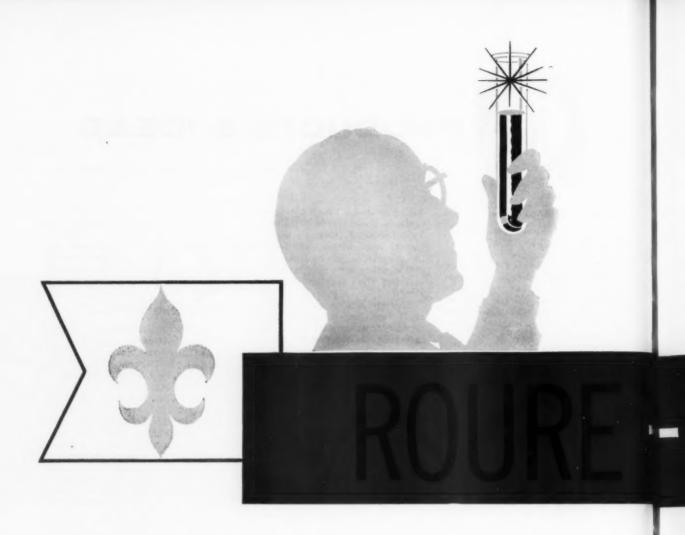
SPECTROPHOTOMETER-3

A new prism-grating infrared spectrophotometer, reportedly the first fully automatic continuous scanning instrument of the grating type, is now available from Beckman Instruments, Inc.

spectrophotometer, The Beckman IR-7, offers high resolution, variable scanning speed, repetitive scanning, horizontal stripchart recording with variable abscissa and ordinate expansions, convenient switching from doublebeam to single-beam operation. and many other features which make the instrument particularly useful for molecular structure studies. The Beckman IR-7 utilizes a replica grating in conjunction with a sodium chloride prism, and is said to provide three times as much resolution as is possible with conventional double-beam, doubleprism spectrophotometers. addition it features a unique order changing system which permits continuous scanning from 650 to 4000-1 (wavenumbers) and preserves linear wavenumber presentation.







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AEROSOLS

1305: NAIL HARDENER

Q. We are very much interested in obtaining a formula for a nail hardener and nail polish remover. If you have any information that might be of assistance, it will be greatly appreciated. We very much enjoy reading your information-packed editions. C. C. S., Fla.

A. Ingredients potentially useful as nail hardeners were discussed in the AMERICAN PERFUMER AND AROMATICS, page 27, March 1958 issue. The pH of commercial products runs around 6.7 with a solids content of 10 per cent. A trace of surfactant is present along with formaldehyde, sodium and potassium in some form. Keratin hydrolysates are also suggested as possible starting points for this kind of product. Acetone, methyl ethyl ketone, butyl acetate and toluene are some of the solvents that can be used in any desired ratio as nail polish removers.

1306: ROYAL JELLY

Q. This is a much delayed answer to deNavarre's article on Royal Jelly. The enclosed facts which you have permission to quote or publish in its entirety will give the true story up to the time of its publication to everyone interested in Royal Jelly, and also stop any controversy by anyone unfamiliar with bees and the food of their queen. Y. F. J., Calif.

A. The recent letter from the Canadian Department of Health and Welfare states a position on Royal Jelly that we feel gives the facts as they are known today. It said in part, "A survey of the scientific literature has revealed that a number of analyses of Royal Jelly have been made and investigations conducted on its possible therapeutic value for humans. However, to date no conclusive results have been reported. In view of Section 9 (1) of the Food and Drug Act... Objection is taken to any claims whatsoever being made for this substance until satisfactory clinical evidence is submitted to substantiate them. Up to the present, no such evidence has been presented..."

1307: EMULSIFIER

Q. I used Aquaphor as an emulsifier in my last batch of face cream. It coarsened the texture of that cream, which before had had such a satiny texture. I knew I had to have an emulsifier, and this is the result with the first emulsifier used. The very finest emulsifier obtainable is demanded for this cream. What about Spans or Tweens? My formula is a solidified oil with not too much aqueous substance. Is this what is known as a water-in-oil formula? If the aforementioned emulsifiers could be used, should it be Span or Tween or both? A beginner is truly lost in a forest of emulsifiers when he finds twenty-eight manufacturers of such listed in the Drug & Cosmetic catalog. I appeal to you to help me Anhydrous lanolin, tallow, coco butter and petrolatum form the base. What is the meaning of pH? S. P. S., Conn.

A. We cannot give you very much help unless we know the formula for your product. If you care to send a copy of the formula, we will be glad to try to make suggestions or changes such as are mentioned in your letter. We further suggest that you get yourself a book on cosmetics which will explain many of the facts about raw materials and their effect in products as well as give you the story behind pH. There are two such books now available from the book department of the AMERICAN PERFUMER AND AROMATICS; namely, "Modern Cosmeticology," by Ralph G. Harry and "Cosmetics: Science and Technology," by Edward Sagarin, et al. pH in simple language is the degree of intensity of acidity or alkalinity of a product.

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Insecticides are always well to the fore when considering aerosol sales. Such products are designed to destroy insects but commodities for use as simple repellents are less well known. In the home, repelling the offending insect is of little value, but out of doors it is a different matter. I have often been asked for information on insect repellents for use in cosmetics both aerosol and normal types. Anyone interested in such products should read H. F. Pierce's article in Soap and Chemical Specialties' June 1958. This paper describes diethyltoluamide as "the best all-purpose insect-repellent so far." It deals with the chemical, physical and repellent properties and especially with its adaptability to pressure packaging. The commercial product consists of 85 to 90% meta isomer and may have the following characteristics:

1. Virtually water white.

 A characteristic mild odour, but completely free from impurities causing off odours.

3. Moisture content of less than 0.5%.

4. Acid No. less than 0.15.

5. Refractive index, approximately 1.52.

6. Specific gravity at 25/25°C. ap-

proximately 1.0.

Cosmetic grades are available and are said to possess the important properties of non-greasiness. Even in concentrated form it will produce a non-oil uniform layer on the skin. When sprayed from an alcoholic solution it dries immediately, yet repels for hours. Laboratory studies show that its order of toxicity is in line with such repellents as dimethylphthalate and ethyl-hexanediol. Like other repellents it may have some solvent action on certain plastics.

Diethyl-toluamide has been used in alcoholic solution in stick form and in aerosols and can be used in combination with a sun-screen product. Further, it appears to be compatible with emulsions. Treatment of clothing via the pressure techniques is advocated and protection is said to be given for days or even weeks (in the absence of washing). When packed in aerosol form a wet spray is desirable and the amount of diethyl-toluamide recommended is 15%. For use on the skin an equal amount of ethyl

* Chief Chemist, Polak & Schwarz, England, Ltd.

alcohol is suggested. The propellant suggested is dichlorodifluoromethane or mixtures of this and trichloromonofluoromethane. Impressive figures for repellency are given, resistance to rinsing in water is said to be high and the product is not easily removed by rubbing. Cornoin problems do not arise if the acid number is low.

It is always interesting to see a new name in the literature especially when the subject matter includes aerosols. N. S. Peel has written in the June edition of 'Soap, Perfumery and Cosmetics.' It seems to me Mr. Peel is much too well informed to be a new-boy. I sense the style of my very good friend Freddie Wells. Anyway, the article is of interest to the pressure packaging people and has a lot to say on the recent discussions on the possible dangers of high polymers in hair-sprays. Aerosol cosmetics are discussed and formulae given for antiperspirants, hand creams and suntans: the latter, in various forms.

Do you pack or intend packing antiperspirants or personal deodorants? If so, Blank, Jones and Gould (American Perfumer, July 1958) have something to interest you. They have made a study of the Penetration of Aluminium Salts into Excised Human Skin. Likewise, Fredell and Longfellow have evaluated antiperspirant and deodorant products in

the same edition.

DuPont's "Aarosol News" is always welcome. The Spring edition mentions a pycnometer for the determination of propellant compositions. It describes a novel aerosol product capable of inflating an average sized tire. Of interest is their comment on a new adhesive bonding agent. It is non-irritating, dries in a few minutes and does not seal skin pores. In lighter vein, toys actuated by propellants are described. These include boats, rockets and missiles. No one admires the efforts of the DuPont organisation (insofar as they concern aerosols) more than I, but honestly, I found their explanation of the relationship between Freon" number and chemical composition, both confusing and complicated.

The preparation of emulsions for use under pressurized conditions presents a number of difficulties. In fact, the dispensation of an emulsion in non-areated form by means of the liquefied propellants is almost impossible. Although the

compressed gases offer greater possibilities there remain several problems to overcome. In any case, whether the emulsified product is to be pressure or nonpressure packed you need a sound fundamental approach to formulation. For this reason, I found the 'American Perfumer' June, 1958 articles of special interest and value. Basic Emulsion Technology by P. J. Carter, Triethanolamine Emulsions by P. G. I. Lauffer, Lanolin Derivatives by L. I. Conrad and special formulation by M. G. deNavarre, all these give extremely helpful advice to the researchers on aerosol emulsions. On the more specialized side, are articles on the effect of perfume oil on emulsions (W Wynne) and a very valuable contribution by G. Kempson-Jones on the Mechanical Treatment of Emulsified Products. To top this important series is a section on Aerosol Emulsions by M. J. Root. I particularly like finding a series of articles on the same subject all in one journal edition

Although one gets a tremendous amount of enquiries for help on various aspects of aerosols, the request that ocsuppliers of laboratory equipment. It is, of course, possible to find such names in the advertisements, but it seems from the enquiries that the needs are not being completely met. For this reason, I was pleased to receive a visit from Mr. David Asdell of Aerofill Limited. His com-pany, Churchill Instrument Company Ltd., have taken over from Messrs. I. F. Eyles (Refrigeration) Limited and will, in future, manufacture pressure filling equipment. By pooling their existing experience in the manufacture of laboratory equipment they are working in association with I. F. Eyles (Refrigeration) Limited as their Sole Agents on the selling of cold filling plant which they will continue to manufacture at Stroud This means they will have a good coverage of machinery likely to be required by the aerosol industry.

The existing Eyles machine has been modified and improved. Aerofill Limited claim that one of the improvements is a finish that will be resistant to materials used in aerosol packaging. Further, the valve head has been improved so that a more speedy fill can be made with the

standard valves.

They have commenced the manufacture of a bottle cap spinning machine, a crimping machine, a laboratory shaker-gasser, a laboratory nitrogen filling machine and equipment for measuring the air flow through nozzles and also, a new range of testing tanks. The present concentrate filling machine has been modified so that in one of its forms it can have P.T.F.E. seals which are fully resistant to any materials likely to be used in the aerosol industry.

In the future, they hope to produce a fast nitrogen filling machine suitable for fitting onto existing plant lines. Also under consideration is a modified version of the standard pressure filling machine

suitable for filling butane.

This new set-up seems a very welcome addition to the limited number of people who can cater for the various people interested in aerosols.



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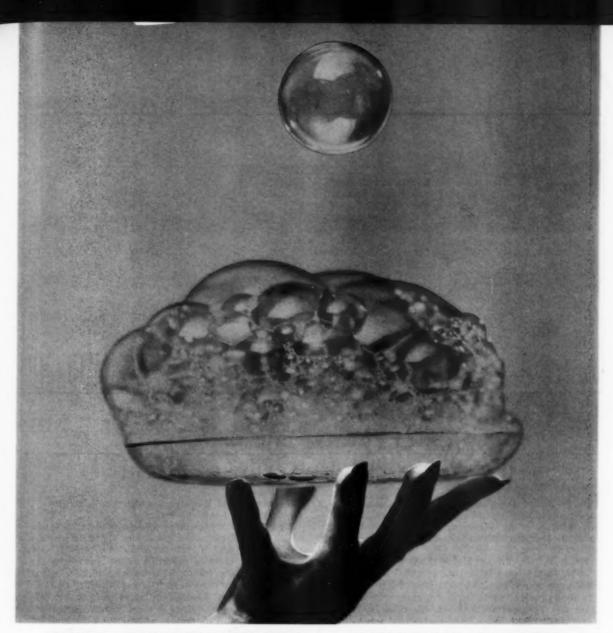
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THE COMMERCIAL SURFACTANTS

M. G. de NAVARRE

About twenty-five years ago commercial surface active agents were first introduced to the toilet goods industry. Hundreds of compounds of four main types have been introduced since that time. Soap has largely been replaced in both commercial and home cleansing operations, to the point where the time-honored toilet bar is now available in "detergent" form.

In 1950 General Aniline and Film Corporation coined the term surfactant to describe synthetic surface active agents used in cleaning and detergent operations. The term is now quite widely used to describe these materials

In the symposium that follows, it is fitting that a contribution from Deutsche Hydierwerke introduces the alkyl sulfates since they were the originators of these materials.

Each contributor was asked to supply four formulas with their manuscript. Some were received with a great many more, hence had to be deleted at the editor's option.

It is hoped that those chosen for publication will give a diversified group of suggested formulations.

We could find nothing better to give an over-all sketch of surfactants than a paper by G. M. Gantz contributed to another journal in 1956 and reprinted by permission with additional notes from the author.

Excluding soap, the sequence of papers is as follows:

Sulfonated Oils
Anionic Surfactants
Cationic Surfactants
Ampholytic Surfactants
Nonionic Surfactants

We offer two contributions on ampholytes, which give as many approaches to this newly stimulating field of surfactants.

While not the alpha and omega of surfactant usefulness, the Ross-Miles tests published by Sanders in 1951, give a group of useful data.

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		1	Foam Hei	ght (mm.)
% Activity		Distille	d Water		p.p.m. Water
Surfactant as Marketed	Type	0 min.	5 min.	0 min.	5 min.
Miranol HM 40	Lauryl Imidazoline	. 220	215	120	110
Duponol WA Paste 31	Sod. Lauryl Sulfate		200	125	120
Ultrawet K 85	Sod. Alkaryl Sulfonate		195	225	220
Arctic Syntex M 32	Sod. Monoglyceride Sulfate		195	205	200
Antaron K460 60	Sod. Alkaryl Polyglycol Sulfate		185	220	215
Igepon T H.C 72	Sod. Oleyl Taurate		195	170	170
Maypon 4C 35	Oleic-Protein Condensate		170	155	145
Ninol 128 100	Amine Condensate		165	45	35
Pot. Coconut Soap 15	************************************	160	150	15	10
Onyx BTC 50	Quaternary	190	70	190	20
Aerosol OT 100	Sod. Dioctyl Sulfosuccinate	180	15	50	15
Brij 35 100	Lorol Polyglycol Ether	120	110	95	85
Nekal BX H.C 80	Sod. Dibutyl Naphthalene Sulfonate		25	180	15
Triton X100 100	Alkyl Phenol Polyglycol Ether	125	75	115	60
Tergitol 4 25	Sod. sec-Alcohol Sulfate		5	90	5
Tween 20 100	Sorbitan Monolaurate Polyglycol Ether		75	80	70
Monosulph 68	Sulfonated Caster Oil	90	30	20	0
Sterox CD 100	Tall Oil Polyglycol Ester		30	35	30

Note: Run at 0.1% active ingredient at 30° C. From H. L. Sanders, Soap, December, 1951.

Supplementing the data is additional material of cosmetic value such as are found in the "Proceedings of the Scientific Section of the Toilet Goods Association," and "The Journal of the Society of Cosmetic Chemists."

F. D. A. Surveying Labeling of Flavoring Products

The Food and Drug Administration is conducting a survey of the labeling of extracts and flavors. In connection with this the Flavoring Extract Manufacturers Assn. has issued a bulletin the significant parts of which follow:

Dr. J. W. Sale, former chief of the Beverage Inspection division in the years 1939, 1940 and 1941, addressed the association regarding interpretations of Section 403 (i) (2) that provides as follows: "in case it is fabricated from two or more ingredients, the common or usual name of each such ingredient; except that spices, flavorings, and colorings, other than those sold as such, may be designated as spices, flavorings, and colorings without naming each: Provided, That to the extent that compliance with the requirements of clause (2) of this paragraph is impracticable, or results in deception or unfair competition, exemptions shall be established by regulations promulgated by the Secretary."

Dr. Sale's interpretation and application was as follows: "We receive a great many inquiries about the application of this subsection to flavors and other foods. We believe that the act does not contemplate the listing on the labels of food flavors of such chemical names as acetyl methyl carbinol and ethyl oenanthate, as such names cannot be regarded as the common or usual names of these ingredients. On the other hand, the public is more or less familiar with some of the more common synthetic flavors such as vanillin and coumarin, with the various essential oils such as fennel, cinnamon, clove, bitter almond, etc., with true flavors derived from plant material or fruits such as maple flavor, strawberry flavor, etc., and with such usual ingredients of flavors or imitation flavors as sugar, water, alcohol, glycerol, phosphoric acid, citric acid, and tartaric acid. We are of the opinion that all such substances with which the public is more or less familiar and which are defined in dictionaries should be listed by their specific names on the labels of food flavors and imitations which are subject to the requirements of this subsection.

The listing of the other ingredients referred to above which bear complex chemical names and with which the public is unfamiliar, can serve no useful purpose and such names cannot be regarded as the common or usual names of the ingredients within the meaning of the Act. Under these circumstances it is not our purpose to take regulatory action against imitation food flavors which describe such constituents as ethyl oenanthate and other esters bearing unfamiliar names, diacetyl and other ketones bearing unfamiliar names, and heliotropin and other aldehydes bearing unfamiliar names, as artificial flavor consisting of synthetic esters, ketones, and aldehydes. Vegetable extractives bearing unusual names such as phoenugreek, lovage, Balsam poplar buds, Balm Gilead buds, etc., may properly be described as extractive matter from seeds, roots, bark, etc.

"The other constituents referred to above which bear such common or usual names as vanillin, coumarin, clove oil, coffee, licorice, malt, cocoa, sugar, water, phosphoric acid, etc., should be listed by their specific names. Such of these ingredients as are artificial flavors should be described as such."

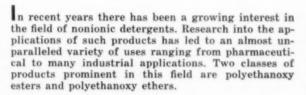
The aforesaid interpretation and application of Dr. Sale has not been adhered to by the flavoring products industry. Many manufacturers are not labeling imitation extracts and/or flavors in accordance with aforesaid interpretation and application.

The Department is now of the opinion that this practice be remedied and the specific ester, predominantly contained therein, be named, with the qualifying term, "and other esters." The predominant ketone and other ketones must be listed, etc.

The Department has likewise criticized the flavoring products industry regarding the labeling of vanilla extracts fortified with vanillin.



POLYETHANOXY ESTERS and ETHERS



Polyethanoxy Esters

Polyethanoxy esters are condensation products of a hydrophobic acid and polyethylene glycol or ethylene oxide. The number of combinations of hydrophobic and hydrophilic compounds in the polyethanoxy ester class of compound is extensive and it is, therefore, only possible to select some of the better known products, to demonstrate the versatility of these esters.

There are two methods for the preparation of polyethanoxy esters; one is to react the hydrophobic acid with ethylene oxide in the presence of an alkaline catalyst and the second is to esterify the acid with polyethylene glycol in the presence of an acid catalyst. It is important to note at this point that the products of either reaction are not pure compounds but are in fact mixtures of at least three components: mono-





B. MILLING

The author has been with Marchon Products Ltd., White-haven, England, for five years as a research and development chemist. During the first three years he was concerned with process development of detergent raw materials and since then he has controlled the investigation in the application of the various products manufactured by Marchon Products, Ltd.

esters, diesters and free polyethylene glycol.1 The esters themselves are also mixtures of varying chain lengths, the distribution of which is similar to that shown in the ethers-which is discussed later. A study of the ethoxylation of lauric acid with 10 molecules of ethylene oxide has shown that under equilibrium conditions the ratio of the concentrations of monoester:diester:free glycol is approximately 2:1:1 respectively. Thus the nomenclature of a commercial polyethanoxy ester refers to the molar proportions used in the reaction mixtures and not to pure compounds: the example given above is described as lauric acid 10 mole ethoxylate. The polyethanoxy esters prepared by the esterification of fatty acid with polyethylene glycol are generally termed polyethylene gylcol x monoester, where x refers to the molecular weight of the polyethylene glycol used. Therefore an alternative nomenclature for lauric acid 10 mole ethoxylate would be polyethylene glycol 440 monolaurate.

Possibly the most versatile series of polyethanoxy esters are those prepared from lauric, stearic and oleic acids. Some of the physical properties of a typical series of polyethylene gylcol derivatives of these fatty acids are given in the following table:

					SOLUI	BILITY	
ESTER	GLYCOL	TRADE NAME*	APPEARANCE	Water	Min. Oil	Neut. Oil	Oleic Acid
Monolaurate	PEG.400	Empilan AQ100	Liquid	8	i	sls	sls
Mono-oleate	PEG.400	Empilan BQ100	Liquid	Disp	sls	sls	sls
Monostearate	PEG.400	Empilan CQ100	Paste/solid	Disp	sls	sls	sls
Monolaurate	PEG.1500	Empilan AP100	Paste/solid	8	i	i	i
Mono-oleate	PEG.1500	Empilan BP100	Paste/solid	8	i	i	i
Monostearate	PEG.1500	Empilan CP100	Paste/solid	8	i	i	i

s-soluble, sls-slightly soluble, disp-dispersible, i-insoluble

* Marchon Products Limited, Whitehaven, England.

Probably the greatest application of polyethanoxy esters is as emulsifiers2 in pesticides, and in pharmaceutical, cosmetic and food stuff preparations, although there are many other general industrial uses. For example, PEG.400 monolaurate is recommended as an emulsifying agent for D.D.T. in commercial solvents. A concentrated solution of D.D.T. can be prepared to the formula 25% D.D.T., 65% xylol and 10% PEG.400 monolaurate, which can be subsequently diluted with water to give an instantly dispersed emulsion for agricultural and household sprays. In cosmetic preparations PEG.100 monolaurate has been recommended as an emulsifying agent for perfume and essences. PEG.400 monostearate is used to suspend zinc oxide in aqueous media in the preparation of creams, etc. PEG.1500 monostearate and PEG.400 monostearate are used for the preparation of lotions: for example a stable emulsion of Benzocaine can be prepared with these products. It has been found that incorporating 1% of PEG.400 monolaurate improves the consistency of edible gelatin.

Many industrial applications of PEG.400 monolaurate have been discovered. The excellent wetting properties of the product make it an ideal wetting agent for dust suppression, and in the dyeing industry where good penetration is required. PEG.400 monolaurate has good lime soap dispersion properties which enables it to be used for general cleansing and scour-

ing purposes.

A study of the detergency properties of polyethanoxy esters³ has shown that optimum detergency is achieved when the mean number of ethanoxy units condensed with the fatty acid is two-thirds the number of carbon atoms in the fatty acid chain. It has also been shown that soil removal is at a maximum and soil redeposition at a minimum with polyethanoxy laurate, compared with polyethanoxy esters derived from other pure fatty acids.

Polyethanoxy esters of Tall Oil⁴

Tall oil is an economical source of unsaturated fatty acids, and is widely used, refined or distilled, as the feedstock for the preparation of polyethanoxy esters. These are prepared by many manufacturers, among which are Monsanto Chemical Company (Sterox C.D.), Atlas Powder Company (Renex 20), Blockson Chemical Division of Olin Mathieson (Teox 120) and Ar-

mour and Company (Energetic).

The tall oil ethoxylates have good stability towards acids and alkalies and are recommended for incorporating in low sudsing detergent compositions and for textile scouring. The problem of incorporating the liquid tall oil ethoxylate in powder products can be overcome by mixing with urea, whence a free flowing powder is obtained which can then be compounded with alkalies, etc. (Renex 25). The tall oil ethoxylates with the necessary hydrophilic-hydrophobic balance are used as emulsifiers in systems containing aromatic solvents and chlorinated hydrocarbons. Their detergent properties enable them to be incorporated in detergents suitable for general household uses, hard surface cleansers and carpet shampoos.

Polyethanoxy Ethers

Polyethanoxy Ethers can be conveniently subdivided into two classes: ethers derived from the reaction of ethylene oxide with an alkyl phenoxy feedstock and ethers derived from a fatty alcohol feedstock. Commercial polyethanoxy ethers are mixtures of ethers of varying chain lengths^{6,6} the distribution of which has been shown to be represented by the Poisson formula, that is the proportion of an ethoxylate chain length c is given by $\frac{c^{-m} \times m^c}{c^i}$ where m is the mean chain length. This is assuming ethoxylation takes place on the hydroxyl group only.

Polyethanoxy Alkyl Phenol Ethers

Alkyl phenol ethers are prepared by reacting alkyl phenol or alkyl cresol with ethylene oxide, in the presence of an alkaline catalyst, to the required hydrophobic/hydrophilic balance. The parent alkalates mainly used for the preparation of these nonionic detergents are octyl phenol, nonyl phenol, dinonyl phenol, dodecyl phenol and octyl cresol. Because of the large consumption of alkyl phenoxy ethers there are many manufacturers both in the United States⁷ and in Europe.

Alkyl phenols react with one or more molecular proportions of ethylene oxide according to the equation:

$$C_8H_{17}C_6H_4\cdot OH + n CH_2 - CH_2 = C_8H_{17}C_6H_4 (OCH_2\cdot CH_2)_n\cdot OH$$
octyl phenol

The lower members of the series are only sparingly soluble in water and are considered to be antifoaming agents. They can also be used in the preparation of quanternary ammonium compounds such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, which is a cationic germicide alleged to be effective against slime producing organisms. The water solubility of the alkyl phenoxy ethers increases as the number of ethoxy groups increases, and solubility can be used to give an approximate measure of the extent of ethoxylation. The melting points of the alkyl phenoxy ethers increase with increasing extent of ethoxylation: 2 to 10 mole adducts are liquids, 10-20 mole adducts pastes and the higher ethoxylated adducts waxes.

The 4-10 mole ethoxylates are considered to be good emulsifying agents and efficient detergents. The 6 mole adduct is recommended for wool washing, the 9 mole adduct for washing feathers and the 10 mole adduct for washing cotton. Being chemically stable towards alkalies the alkyl phenoxy ethers have been used to replace soap in laundry practices.

One of the largest applications of alkyl phenol ethoxylates is as an emulsifying agent, and it has been shown that the mixed ethoxylates obtained by normal manufacturing techniques have superior emulsifying properties over the pure compounds obtained by fractional distillation of the commercial material.

The lower members of the alkyl phenoxy ethers can be sulphated to give anionic detergents (Alipal CO series of products¹⁰) which are used in light duty household liquid detergents and many other liquid detergent formulations.

Polyethanoxy aliphatic ethers

Polyethanoxy aliphatic ethers are prepared by reacting such feedstocks as propylene glycol, fatty alcohols, oxo alcohols and various waxes with ethylene oxide in the presence of a catalyst. Many manufacturers prepare polyethylene series of derivatives of one or more of the above, and the author has chosen one or more at random, as examples of each group.

Polyethanoxy polyoxypropylene glycol ethers example Pluronics¹¹

These are 'block polymers' prepared by condensing

ethylene oxide with polyoxypropylene glycol of molecular weights ranging from 800 to 2,500.

The application of these compounds depends on their hydrophobic/hydrophilic balance, which is a function of the extent of ethoxylation. Owing to their low foaming characteristics they can be incorporated in controlled foam laundry detergents and also in machine dishwashing compounds.

Polyethanoxy ethers of fatty alcohols Empilans and $\operatorname{Empicola}^{13}$

As it is possible to prepare ethylene oxide adducts of all the fatty alcohols, and an almost infinite number of combinations is possible. Thus it is necessary to choose the cheapest available raw materials for the properties required. Commercial oleyl alcohol ethoxylates are widely used as emulsifiers. For example, a series of products prepared under the trade name Empilan KL. has many industrial and cosmetic applications (see table).

Product	Appearance	Applications
Empilan KL. 2	Liquid	Emulsifier for hand & hair creams Emulsifier & stabil- izer in emulsion paint
Empilan KL. 6	Liquid/paste	Emulsifier for hand & hair creams Emulsifier and stabilizer in sprays for agricultural application, insecticides, fungicides, etc Emulsifier for paints Emulsifier for metal cutting & drilling oils
Empilan KL. 10		Mineral oil emulsi- fier for the textile industry Batching oil emul- sifier for Flex, Jute and Sisal Emulsifier for metal cutting oils
Empilan KL. 20	Soft Wax	Oleic emulsifier for textile applications and in particular for the woolen in-

Commercially lauryl alcohol ethoxylates are recommended for emulsifying and stabilizing creams and ointments for pharmaceutical application. ¹⁴ They have also been shown to be useful additives when used in conjunction with soap in toilet bar preparations; ¹⁵ for example, lime soaps can be dispersed more readily, thus making the toilet bar more economical in hard water. Homogenity and texture are improved, rancidity is reduced, and perfuming enhanced, when lauryl alcohol ethoxylates are incorporated in toilet bars.

dustry.

It is possible to sulphate the lower polyethanoxy lauryl ethers, 3 mole adduct and lower, to produce anionic surfactants which all have a high degree of foaming power. This and the fact that the foam does

not readily collapse in the presence of soap has resulted in their incorporation in foam bath preparations. The lauryl ether sulphates have some advantages over sodium lauryl sulphate and in some cases the ether sulphates are replacing the alcohol sulphates in liquid detergents and shampoo formulations.

The physical characteristics and foaming power make the lauryl ether sulphates particularly adaptable to shampoo formulations, examples of clear liquid types are as follows:

p	deneral durpose nampoo	For 'Dry' Hair	For Oil or Greasy Hair
Empicol SLE	33	33	33
Empilan C.Q. 100	-	2.0	
Oleyl Alcohol	0.25	_	_
Isopropyl Alcohol	0.25	-	-
Sodium chloride	_	2.25	6.0
Perfume	q.s.	q.s.	q.s.
Colour Water	q.s.	q.s. Balance to 10	q.s.

Lauryl ether sulphates have excellent cloud points, good solubilizing action for other ingredients, and their viscosity can be controlled by the addition of sodium chloride up to a jelly consistency. Empicol SLE.1 and SLE.2 are typical lauryl ether sulphates and the following viscosity characteristics have been observed:

%			
EMPICOL	RANGE OF	RANG	E OF NaC1
SLE.1 or 2	VISCOSITY	RE	QUIRED
		Empicol SLE.1	Empicol SLE.2

25%	1000-5000	centistokes	7.0-9.0%	4.0-5.9%
33%	2000-14000	00	5.5-9.0%	3.5-5.0%
50%	5000-30000	00	4.25-6.75%	2.25-4.25%

The sodium lauryl ether sulphates are also used in the preparation of household liquid detergents. Although they can be used alone, they normally form the anionic component in binary or ternary mixtures incorporating nonionic detergents and foam stabilizers.

Polyethanoxy tallow alcohols

Bistline et al¹⁷ have studied the properties of the sulphated polyethanoxy tallow alcohols and have shown that the 2 mole adduct sulphate has detergency properties equal to those of the corresponding alcohol sulphates. The 10 mole adduct sulphate is more soluble but is a less effective detergent. It has however greater stability with regard to metal ions and to acid hydrolysis. All the products were shown to have good line soap dispersion and good emulsifying properties.

Polyethanoxy OXO alcohols

The reaction mechanism of the ethoxylation of OXO alcohols has been studied in some detail. Commercially tridecyl alcohol ethoxylates are the most popular of this group of compounds and these are currently being manufactured by Antara Chemicals, Division of General Aniline & Film Corp. (Emulphogenes). The Atlas Powder Company (Renex 30) and Olin Mathieson (Polytergents J series). Good wool and cotton washing efficiencies are claimed for these products; for wool washing they can be used in acid media to minimize felting, and for cotton washing may be compounded with builders and anionic surfactants such

as alcohol sulphates and alkylaryl sulphonates. Its compatibility and good solubilising properties with anionic detergents make polyethanoxy tridecyl alcohol a useful ingredient in light duty liquid household detergents.

The 6 mole ethoxylate is not very soluble in water but is soluble in organic solvents, thus making it a useful wetting agent where oil contaminated fibres, fabrics and solid surfaces must be wetted out. It can also be used as a wetting agent in paints, polishes and wood stains, making the application of such products more speedy and the resulting finish more uniform. The emulsifying properties of the 6 mole ethoxylate are good but in many cases this can be enhanced by admixture with higher ethoxylates.

The 8 to 10 mole ethoxylates are more soluble than the lower members and at this level of ethoxylation the foaming properties improve, bringing it into the class of product suitable for incorporation in household detergents. The versatility of this type of material as a wetting agent is demonstrated by its use in the paper industry, metal pickling, oil well acidising, insecticidal powders, glue industry, paint washing solutions, latex paint emulsion and general degreasing compounds.

Ethoxylated tridecyl alcohol containing more than 10 moles of ethylene can be used in general cleansing compounds, are good lime soaps dispersants and good wetting agents thus making them useful additives for dyeing baths. They are also claimed to be good emulsifiers for fatty acids and natural waxes, and good solubilisers for such water in soluble oils as vitamin oils, perfume oils and chlorinated insecticides.

Polyethanoxy ether-esters

A typical series of such products are the Tweens,19 which are prepared by reacting a poly-ol of the sorbitol type with ethylene oxide to produce a hydrophilic ether, which in turn is condensed with a hydrophobic acid to produce a surface active etherester.20 The properties of some of the Tweens are given in the following table:

Trade Name	Composition Physical Form	Application
Tween 20	Polyoxyethylene Liquid sorbitan mono- laurate	General emulsifier and solubiliser for essential oils and vitamins
Tween 21	Polyoxyethylene Liquid sorbitan mono- laurate	Wetting agent Lower EtO content than Tween 20
Tween 40	Polyoxyethylene Liquid sorbitan mono- palmitate	General emulsifier
Tween 60	Polyoxyethylene Liquid sorbitan mono- stearate	General emulsifier —particular appli- cation for food- stuffs
Tween 61	Polyoxyethylene Solid sorbitan mono- stearate	General emulsifier. Lower EtO content than Tween 60
Tween 65	Polyoxyethylene Solid sorbitan tris- tearate	General emulsifier —particular appli- cation for food- stuffs
Tween 80	Polyoxyethylene Liquid sorbitan mono- oleate	General emulsifier and solubiliser for essential oils

Conclusion

The reader will appreciate the immensity of the field of the polyethanoxy esters and ethers, and as it is impossible to consider each individual product the author has attempted to enumerate the more important types of compounds at present on the market and discuss their properties and applications. Their relative inertness towards acids and alkalies, ease of handling, compatibility with other surfactants, together with their characteristic performance qualities, have stimulated many manufacturers to enter this field, and it is certain that their scope will continue to expand in the future.

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Fill-In Orders

Some years ago one company tried the experiment of declining all orders of less than break-even size. Six months later they hastily reinstated the old practice. They were losing too many big orders from customers whose trifling fill-in orders between seasons they had turned away. Admittedly, there is a point at which you must stop losing money. But sometimes you must lose a little here to make a great deal there.-Rogers, Slade & Hill.



'I want a sun-tan lotion that has no effect on beneficial, bactericidal and therapeutic rays!





STRUCTURE and PROPERTIES SURFACTANTS

George M. Gantz is program manager of Application Researc's and Technical Service, Central Research Laboratory, General Aniline & Film Corp. One of his special interests has been the development of surfactants. He was senior chemist of the Naval Research Laboratory from 1940 to 1946 after which he was research director until 1951 for the Lonsdale Co. From 1951 to 1954 he was product engineer for the General Aniline & Film Corp. and then supervisor until 1957 of the Technical Dept., Antara Chemicals Division, General Aniline & Film Corp. and subsequent to that supervisor of the New York Laboratories of the division. He is a member of the ACS, AAAS, TRI and of the honorary scientific society of Sigma XI.

G. M. GANTZ*

Soap is the oldest surfactant, perhaps 2,000 years old, and until very recently dominated the field. Synthetic detergents or surfactants are more than 100 years old but they were insignificant until a shortage of soap in Germany during World War I sparked their development.

After the war, a tremendous number of synthetic detergents were made and patented, particularly in Germany. The greatest application for these new products occurred in the textile industry. By the end of World War II it is estimated that production and consumption of synthetic detergents in this country was 90-100 million pounds per year. This was still small compared to an annual soap production of three billion pounds.

Starting in 1945 a very marked growth occurred in synthetics and by 1947 soap sales began to decline. This is shown in Figure 1. Built detergents based on synthetic surfactants continued to displace soap powders until synthetics surpassed soap in 1953. Most evidence points to a continuation of this trend.

As might be expected, the marked growth of synthetic surfactants since the war prompted more and more research and development by the chemical industry. An increasing number of new surfactants is being patented and very large numbers of tradename products are offered for sale.1, 2, 3 It is becoming much more difficult, therefore to classify and discuss surfactants.



Source: 1953-54-Association of American Soap Producers; 1955-62-J. Ralph Macon, The Atlantic Refining Co.
Reference: Chemical Week, Oct. 22, 1955, p. 40.

Figure 1-Soaps vs. synthetic detergents. The balance tipped in 1953

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The registered trade-names used in this paper include: "Ethemid"—Armour & Co.; "Span" and "Tween"—Atlas Powder Co.; "Tergitol"—Carbide & Carbon Chemicals Co.; "Gordinels" and "Dupenels"—E. I. du Pont de Nemours & Co.; "Igepal CO" and "Igepan"—General Aniline & Film Corp.; "Miranol"—Miranol Chemical Co.; "Ninol"—Ninol Laberatories; "Orvus"—Procter & Gamble Co.; "Triton"—Rehm & Heas Co.; and "Pluronic"—Wyandotte Chemicals Corp.

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General Nature of Surfactants

The theory of surfactants has been studied and developed as an important part of the field of surface chemistry. The contributions of Adam, Alexander, Harkins, and McBain plus many other eminent colloid chemists, have led to a much better understanding of the physicochemical properties of surfactants.

Concurrently with the scientific studies of surfactants by chemists, physicists, and biologists, a vast technology has developed related to the application of surfactants in many different industries. This work includes studies of the effect of surfactant structure on wetting, detergency, emulsification, dispersion of pigments, and foaming. Unfortunately, a large gap exists between our scientific knowledge and our practical knowledge. When one is confronted with a practical problem involving surfactants, it is quite often necessary to try a great many of the products available. Correlation of molecular structure with surface activity and performance in specific applications is a fruitful field and one may expect more work of this type.

A surfactant may be defined as a material which will greatly reduce the surface energy of a solvent at a very low concentration. A good wetting agent, for example, will reduce the surface tension of water from 72 to 30 dynes/cm. at a concentration of less than 0.01%. In general, surfactants can be defined also as molecules containing a hydrophobic group and a hydrophilic group. Figure 2 illustrates this hydrophobic-hydrophilic balance in sodium laurate, a soap molecule.

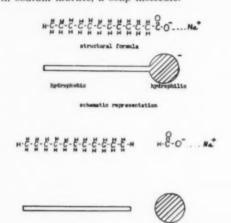


Figure 2-Hydrophobic-hydrophilic balance of sodium laurate

If the molecule of sodium laurate were severed between the 11th and 12th carbon atom, one would obtain n-undecane and sodium formate. As a straight chain hydrocarbon, n-undecane might be found in kerosene or mineral oil. It would be insoluble in water and highly polar solvents but quite soluble in oils. Sodium formate on the other hand is quite soluble in water but oil insoluble. Neither fragment of this soap molecule would have any surface active properties. The unique character of surfactants depends upon the presence of both an oil soluble and a water soluble group within the molecule.

Consider the forces acting upon a single molecule in a solvent such as water (a) when the molecule is in the body of the liquid and (b) when the molecule is at liquid-air interface (Figure 3). In the body of the liquid, cohesive forces will uniformly attract the molecule on all sides. For a molecule at the surface, however, there will be an attractive force down into the liquid so that the surface acts as if it were under compression.



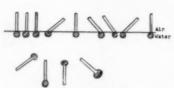


Figure 3-Molecular forces in a liquid and orientation of soap molecules

If a few molecules of soap are added to the liquid, they will tend to collect at the surface. Water molecules have little or no attraction for the hydrocarbon tail of the soap molecule and they get squeezed out and line up at the surface as shown in Figure 3. As more and more soap molecules collect at the surface, the surface tension is reduced until the surface is completely covered with soap molecules.

The quantitative relationship between the degree of adsorption at the surface and the lowering of surface tension was developed by J. Willard Gibbs by thermodynamic methods. For dilute solutions the Gibbs equation can be given as follows:

$$e = -\frac{C}{RT} \frac{d_a}{dC}$$

where e is the excess concentration in the surface layer, a is the concentration in solution. R is the gas constant, T is absolute temperature and $\frac{d_a}{dC}$ is the rate of change of surface tension with concentration.

A typical curve of surface tension versus concentration for a surfactant is shown in Figure 4. The concen-

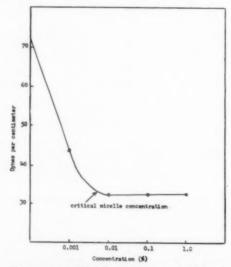


Figure 4-Surface tension of Igepal CO-630 in water at 25°C.

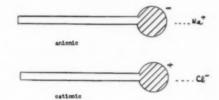
tration at which no further reduction of surface tension occurs is known as the "critical" micelle concentration. When no additional concentration of surfactant at the surface takes place, it must remain in solution. However, surfactant molecules do not diffuse separately throughout the liquid but clump together in micelles.

Surfactant micelles are shown schematically in Figure 5. They may be spherical, lamellar, or even rod shaped. Although the theory of micelle structure is still being developed, their existence is no longer questioned.





Figure 5-Schematic representation of surfactant micelles





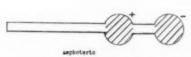


Figure 6 - Schematic representation of surfactant types

Measurements of conductivity, osmostic pressure, as well as both X-ray and optical studies confirm the presence of surfactant micelles. These micelles are believed to be important in detergency, emulsification, and solubilization.

Classification of Surfactants

The majority of surfactants can be classified into four main groups: anionic, cationic, nonionic, and amphotenic. A schematic representation of these types is shown in Figure 6. Anionic molecules are so called because they bear a negative charge and migrate toward the anode or positive pole in solution. Cationic molecules migrate toward the cathode and therefore contain a positive charge.

Nonionic surfactants do not contain an ionizable group and have no electrical charge. The hydrophilic end of this type of surfactant is usually made up of several hydroxyl groups or ether linkages. As indicated in Figure 6, the hydrophilic part of a nonionic molecule is usually larger than that of anionics or cationics and may even be much larger than the hydrophobic part of the molecule.

Amphoteric surfactants contain both a positive charge and a negative charge. These changes may neutralize each other so that at a given pH, the surfactant behaves as if it were nonionic. These surfactants usually exhibit cationic properties in acid solutions and anionic properties in alkaline solutions. Although amphoteric surfactants have been known for a long time they have become commercially important only recently.

Many classification systems have been devised to cover surfactants. Perhaps the most comprehensive system is that devised by Schwartz and Perry in their book on surfactants.4 The classification shown in Table 1 is by no means comprehensive but an effort has been made to include structures which are commercially important.

I-Anionic Surfactants

It will be noted in Table 1 that anionic surfactants include just three hydrophilic groups: carboxyl, sulfate ester, and sulfonic. Although anionic surfactants containing a variety of other solubilizing groups have been made and patented, none are believed to be of commercial importance except the phosphate esters. The phosphate esters are expected to become more important in the future. In addition to good emulsifying properties, they are particularly useful as antistatic agents for textiles and plastics.

A. Carboxylic Acids: The fatty acid soaps will not be considered in any detail. They are made by saponification of natural fats and oils and the most useful products contain between 12 and 18 carbon atoms. A major drawback of the fatty acid soaps, of course, is their sensitivity to hard water. Rosin soaps and tall oil soaps are also sensitive to hard water but they are quite cheap and are used in many industrial operations where color

Table 1-Classification of Surfactants

I-Anionics

- A. Carboxylic Acids
- Soaps; fatty acid, rosin, naphthenic
- 2. Misc.
- B. Sulfuric Acid Esters
- Alkyl sulfates; alcohols and olefins
- Sulfated oils and esters Sulfated amides and ethers
- 4. Misc. C. Sulfonic Acids
- 1. Alkyl sulfonates
- 2. Alkyl aryl sulfonates
- Sulfonated amides and esters
- D. Misc. Hydrophilic Groups; Phosphates, Sulfamates
- Cationic
- B. Quaternary Ammonium Salts
 C. Amino Amides and Imidazolines
 D. Misc.

- III-Amphoteric
 A. Amino and Carboxyl Groups
 B. Amino and Sulfuric Ester or Sulfonic Groups

C. Misc.

- -Nonionics A. Alkyl, Alkylaryl Ethers and Thioethers
- B. Esters and Amides



and odor are not important. Naphthenic acids are used primarily as their heavy metal salts. The copper salt is a fungicide while the lead, cobalt, zinc, and manganese salts are used as driers in paints and varnishes.

B. Sulfuric Acid Esters (Figure 7): Sulfated fatty alcohols were among the first synthetic surfactants to become commercially important. These products, known by such tradenames as "Gardinols," "Duponols," and "Orvus," are used primarily as detergents in the textile industry, as fine fabric detergents or in shampoos. Fatty alcohols required for sulfating are usually obtained by catalytic hydrogenation or reduction with sodium of the corresponding fatty acids.

Secondary alcohol sulfates can be made by sulfating olefins obtained from petroleum. The secondary alcohol

Figure 7-Sulfate ester surfactants

sulfates marketed under the tradename "Tergitol" are believed to be made, however, by aldol condensation, dehydration, and reduction. Some of the products of this type are particularly good as wetting agents in strong acid, alkali, or salt solutions. In general, sulfate esters are not stable in acid solutions.

Oxo process alcohols produced by the Fischer-Tropsch oxidation of paraffins are growing in commercial importance. These primary alcohols, particularly the tridecyl product, can be sulfated to give surfactants.

Sulfated oils, usually referred to as sulfonated oils, are the oldest synthetic surfactants. As early as 1834 it was dicovered that treatment of olive oil with sulfuric acid then neutralizing with potassium hydroxide produced an oily, water dispersible product very useful in dyeing calico reds. These sulfated triglycerides from various oils became known as Turkey Red oils. Products of this type are still used in the textile industry as dyeing assistants, particularly sulfated castor oil.

Sulfated oils and fats such as tallow are used in the textile industry for finishing yarns and fabrics. They provide surface lubrication and softness.

Many valuable surfactants are produced by sulfating esters such as the methyl, propyl, butyl or amyl oleates or ricinoleates. These products foam more, and are better wetting and rewetting agents than the sulfated triglycerides. Sulfation of the hydroxyl group in a mono or di-glyceride or a gylcol monester produces surfactants useful in household detergents, shampoos, and cosmetics. In general, sulfation of any polyhydric alcohol partially esterified with a fatty acid will yield a surfactant.

A veriety of surfactants can be made by reacting fatty acids with ethanolamines and sulfating the resulting alkylolamides. These products are easly manufactured and have been offered by a number of companies for various textile and industrial uses.

Sulfated ethers represent a fairly recent development in the field of surfactants. Sulfation of the terminal OH group of an alkyl phenol or a fatty alcohol ethylene oxide condensate yields surfactants with good wetting, foaming, and detergent properties. These products are used extensively in the formulation of liquid household dishwashing compounds.

C. Sulfonic Acids: Petroleum sulfonates obtained from the manufacture of while oils are complex mixtures of alkyl sulfonates. These are produced in large tonnages and are used to make soluble cutting oils, textile spinning lubricants, and detergents for motor oils. Alkyl sulfonates can be made also from refined petroleum oils by the Reed-Horn process involving sulfur dioxide and chlorine. Many products of this type were made in Germany during World War II,⁵ and du Pont has pioneered their development in this country. Properties of the alkyl sulfonates are similar to the alkyl aryl sulfonates.

The alkyl aryl sulfonates have attained the largest tonnage among surfactants as a result of their use in packaged household detergents. Alkyl benzene types are most important and vary from xylene sulfonates to trialkyl benzene types (Figure 8). These products are used in a great many applications because they are very low in cost, versatile, and chemically stable. The dodecyl benzene or keryl benzene sulfonate is the most effective type for detergency. Larger alkyl chains reduce solubility while smaller alkyl chains reduce detergency but increase wetting action.

Alkyl naphthalene sulfonates such as the dibutyl or disopropyl products represent another important type in this class of surfactants. They are used in a variety of applications for wetting, detergency, emulsification, and dispersing action.

An interesting class of surfactants is made by con-

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Figure 8-Alkyl aryl surfactants

densing naphthalene sulfonates or alkyl naphthalene sulfonates with formaldehyde. These low molecular weight polymers are extremely useful as dispersing agents. They are used in the manufacture of water dispersable dyestuffs as well as in paints, plastics, and rubber manufacture.

One of the most versatile surfactants is made by condensing fatty acids with n-methyl taurine to give a sulfonated amide. These products, developed and sold by GAF under the tradename "Igepon" have been used extensively in the textile industry for many years and are perhaps more like soap than any other surfactant, yet they have none of the disadvantages of soap. The related esters made from fatty acids and hydroxyethanesulfonic acid developed and sold by GAF under the trademark "Igepon A" (Figure 9) are less stable in hot acid or hot alkali solutions. In recent years these sulfonated amides and esters have found many nontextile applications.

Another important class of anionics is the sulfosuccinic esters developed and sold by American Cyanamid

Figure 9-Sulfonated amides and esters

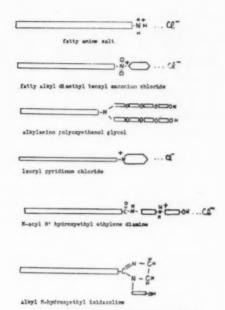


Figure 10-Cationic surfactants

Co. under the tradename "Aerosol" and "Deceresol." These products are made by esterifying maleic anhydride with an alcohol and treating the diester with sodium bisulfite. The sulfosuccinic esters are particularly efficient wetting agents, as Caryl has shown.

II-Cationic Surfactants

Cationic surfactants are used for quite different purposes than the anionics. Perhaps their most unique property is affinity for various surfaces. In textiles they react with many direct dyes (anionic) to improve water resistance, they are powerful softening agents presumably because they orient strongly on individual fiber surfaces. Other important textile uses for cationics are as water repellents, moth proofers, bactericides, and antistatic agents. The major industrial uses are as germicides or sanitizers, corrosion inhibitors, and emulsifiers. Typical structures of cationic agents are shown schematically in Figure 10.

A. Simple Amine Salts: Straight chain fatty amines with 8 to 18 carbon atoms are rather insoluble in water but their hydrochloride or acetate salts have wetting, foaming and detergent properties. Actually these amines are not often used as such but serve as starting materials for preparing more effective surfactants. Reaction of fatty amines with ethylene oxide yields products which are used as emulsifiers and detergents.

B. Quaternary Ammonium Salts: Alkylation of fatty amines with methyl chloride, dimethyl sulfate, benzyl chloride, etc. gives quaternary ammonium salts. These are much more soluble than the amine salts and retain their cationic nature in alkaline solutions. Products of this type are most widely used as germicides. However, a variety of products for special applications fall in this classification. Lauryl pyridium chloride is a spin bath additive in viscose rayon manufacture. Methylolstearamide pyridium chloride is used as a water repellent. Quaternized amine-ethylene oxide types are used as dye stripping agents.

C. Amino Amides and Imidazolines: The majority of textile softeners are made by reacting fatty acids with various polyamines. These amino amides may then be alkylated to eliminate any primary amine group or fully

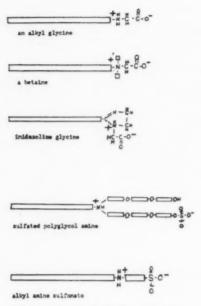


Figure 11-Amphoteric surfactants

alkylated to the quaternary. It is obvious that a variety of complex products can be made and a very large number of proprietary cationic softeners are offered to the textile trade.

By modifying reaction conditions, fatty acids and polyamines will condense to form substituted imidazolines. In general, the imidazolines discolor more on aging or at high temperatures than the corresponding amino amides and have not been used as widely as textile finishes. Quaternized imidazolines also have this disadvantage. Alkyl oxazolines are prepared by condensing fatty acids with amines like 2-methyl-2-amino-1,3 propanediol. Products of this type are marketed by Commercial Solvents Corp. under the tradename "Alkaterge."

III—Amphoteric Surfactants

As noted earlier, amphoteric surfactants, also called ampholytes or ampholytic surfactants, contain both a positively charged and a negatively charged group (Figure 11). The cationic group is usually an amine salt or a quaternary nitrogen. The anionic group is usually a carboxyl, a sulfate ester, or a sulfonic acid. This classification excludes such products as the fatty amine ethylene oxide condensates which may be cationic or nonionic and the alkylolamides which may be anionic or nonionic. The former are considered cationic while the latter are classed as nonionic.

A. Amino and Carboxyl: Reaction of an alkyl amine with chloroacetic acid produces an alkyl glycine with typical amphoteric properties. Further reaction will produce a betaine which contains the quaternary nitrogen group. As might be expected the betaines are more cationic in nature than the simple glycines. A variety of other methods may be used to make both betaines and alkyl glycines from fatty amines.

Reaction of a fatty acid with a polyamine gives an amino amine which can be reacted with monochloroacetic acid to produce an amphoteric product. Likewise the amino amide may first be converted to an imidazoline and then used to make an ampholyte. A number of products marketed under the "Miranol" tradename are claimed to be of this type. The amino amides or imidazolines may be alkylated before or after reaction with

monochloroacetic acid to give betaines. Neu⁹ has indicated that many useful ampholytes have a structure which may be N-alkyl poly (aminoethyl) glycines.

B. Amino and Sulfuric Ester or Sulfonic Groups: Surfactants containing an amino group plus a double bond may be sulfated readily to give an ampholyte. Similarly amino compounds containing hydroxyl groups may be sulfated. The alkyl amine-ethylene oxide condensates contain two terminal OH groups so that one or both might be sulfated. Amino-amides made with hydroxyethyl ethylene diamine or the corresponding imidazolines can be sulfated at the hydroxyl group.

Amphoteric surfactants containing an amino group and a sulfonic acid group can be made by using a halogenated alkyl sulfonic acid in place of monochloroacetic acid. Although many other types of amphoterics containing a sulfonic group appear in the patent literature, it is not believed that any have become commercially important.

Probably the outstanding feature of the amphoteric surfactants is the fact that they behave like cationics without the disadvantage of being incompatible with anionic materials. They are substantive to protein and cellulosic fibers and exhibit softening and lubricating properties. They also have a bactericidal action. Amphoteric surfactants may never become as important as the anionics or nonionics but they should find many applications where cationics would be useful and cannot be used because of incompatibility.

IV-Nonionic Surfactants

The hydrophilic group in anionics and cationics bears an electrical charge and it is usually small relative to the hydrophobic group. The electrical charge must have a marked solubilizing action because the hydrophilic group in nonionics must be quite large if the surfactant is to be water soluble.

An important method of making nonionics involves reaction of ethylene oxide with a hydrophobe group containing an active hydrogen. After one mole of ethylene oxide has reacted with the active hydrogens, further reaction takes place until any desired mole ratio is obtained. This is illustrated in *Table 2*.¹⁰

A. Alkyl, Alkylaryl Ethers and Thioethers: Nonionics made from alkyl phenols were first produced in this country before the war. Their output has continued to rise and their price has continued to drop. Since they are manufactured from phenol, nonene (or diisobutylene) and ethylene oxide, they may be considered as petroleum base surfactants. It is interesting to note that at the present time sales of nonionics are increasing faster on a percentage basis than the alkylarylsulfonates.

A variety of products can be made by adding various amounts of ethylene oxide to an alkyl phenol. There are

Table 2-Preparation of Nonionic Surfactants from Ethylene Oxide

STEPANOL LAURYL SULFATES

Stepanol lauryl sulfates offer you instant solubility, high initial foam and a foam that is creamy...close bodied. They also provide excellent foam stability and free rinsing. These Stepanols are sulfated fatty

alcohols from selected cuts of straight chain alcohols predominantly lauryl. There is a wide variety of Stepanols to meet your requirements for physical form, concentration and inorganic salt content.

TRADE NAME	CHEMICAL DESCRIPTION	PHYSICAL FORM	ACTIVE	FREE FATTY ALCOHOL	CHLORIDE	SULFATE	pH 1% SOLN.	B5./GA1
			ALC: N	1	1995	10	1000	3.9
Stepanol WA Paste	Sodium Lauryl Sulfate	Paste	28-30	1.5-3.0	1.4-1.8	1.4-1.8	7.5-8.5	8.67
Stepanol WAQ	Sodium Lauryl Sulfate	Viscous liquid	28-30	1.5-3.0	0.3-0.8	1.4-1.8	7.5-8.5	8.67
Stepanol WA Special	Sodium Lauryl Sulfate	Clear viscous liquid	28-30	1.0-2.5	0.3-0.8	0.5-1.0	7.5-8.5	8.67
Stepanol ME Dry	Sodium Lauryl Sulfate	Powder	90-94	1.5-3.5	1.0-2.0	1.5-3.5	8.5-11.0	
Stepanol ME Dry AW	Sodium Lauryl Sulfate	Powder	90-95	0.5 Max.	1.0-2.0	1.5-3.5	8.0-10.5	
Stepanol WAT	TEA Lauryl Sulfate	Clear liquid	39.50-41.0	1.3-2.0	1.0-2.0	2.3-4.5	7.0-8.5	8.7
Stepanol DEA	DEA Lauryl Sulfate	Clear liquid	33.5-36.0	1.25-3.25	1.3-2.6	2.6-3.5	8.4-8.7	8.58
Stepanol AM	Ammonium Lauryl Sulfate	Viscous liquid	28-30	1.5-3.0	0.5-2.0	1.5-2.0	5.5-6.5	8.53
Stepanol T-28	Special Sodium Lauryl Sulfate	Viscous liquid	35.5 Min.				9.0	8.6



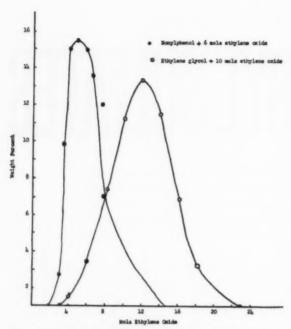
WRITE FOR BROCHURE OF SUGGESTED FORMULATIONS

Included are suggested formulations for a wide variety of liquid, liquid creme and paste shampoos as well as hand cleaner, shaving cream, rug shampoo, and bubble bath formulations.



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FATTY ALCOHOL SULFATES . BULK LIQUID DETERGENTS . ALKYLOLAMIDES . FOAM STABILIZERS . ALKYL PHENOL POLYALKOXY SULFATES . NON-IONIC DETERGENTS . CUSTOM ETHOXYLATION . ALKYL PHENOLS



Reference: R. L. Mayhew and R. C. Hyatt, General Aniline and Film Corp., Journal of the American Chemical Society, Sept. 1952, no. 9, p. 357-362.

Figure 12-Mole ratio distribution of ethylene oxide in polyoxyethylated surfactants

eight nonylphenol products of this type available under the "Igepal CO" trademark varying from a water soluble 4 mole product to a highly water soluble 30 mole product. A similar series of octylphenol nonionics is available under the "Triton" trademark. As the hydrophobic-hydrophilic balance is shifted the surface activity changes. In the nonylphenol series, the most versatile surfactant is obtained with a mole ratio of 8-10.

Surfactants prepared from ethylene oxide are not single compounds but mixtures of compounds with different mole ratios of ethylene oxide. Mayhew and Hyatt¹¹ showed that the composition of a nonylphenol nonionic follows the Poisson distribution formula (Figure 12). Thus the mole ratio for an ethylene oxide nonionic refers to an average value.

Fatty alcohols may be used to prepare nonionics and many products of this type have found specific applications such as stabilization of rubber latices. The Oxo process alcohols may be used to prepare nonionic surfactants with good wetting action and detergency. Alkyl mercaptans such as dodecyl mercaptan react with ethylene oxide to give good surfactants.

A new type of nonionic has been developed recently by adding ethylene oxide to polypropylene gylcol.¹². A polypropylene glycol having a molecular weight of 900 or more is water insoluble and can serve as the hydrophobic base for producing high molecular weight nonionics. Products of this type, marketed under the "Pluronic" tradename, can be produced in a solid form.

B. Esters and Amides: Ethylene oxide reacts with fatty acids (or fats and oils) to yield nonionic surfactants. These esters, however, in contrast to the ethers, are not stable in strongly alkaline solutions. nonionic ester surfactants may also be made by esterifying a fatty acid with a polyethylene glycol. These glycol esters can be made in rather simple equipment and a great many manufacturers offer nonionics of this type. The predominate use for the fatty ester nonionics is in emulsification and textile yarn lubrication.

The tall oil ethylene oxide condensates should be noted because they are produced in large quantities. A built tall oil nonionic is used in one of the popular low foaming household detergents. Tall oil products are cheaper than the alkyl phenol products but they are less efficient in most applications.

Fatty acids may be reacted with polyhydric alcohols such as glycerol, sorbitol, pentaerythritol, and glucose. These esters are sparingly soluble in water but are used extensively as oil soluble emulsifiers. The polyhydric alcohol partial esters may be reacted with ethylene oxide to give water soluble nonionics. Combinations of the partial esters and ethoxylated esters such as those available under the trademarks "Span" and "Tween," can be used for a variety of emulsion problems.

The reaction of ethylene oxide with fatty amines to yield cationic surfactants has been mentioned. Ethylene oxide also reacts with fatty amides to yield nonionic surfactants. Such products available under the trademark "Ethomid" are used primarily for emulsification and dispersing action.

A class of compounds variously known as amine condensates, alkanolamides, or Kritchevsky compounds and available under the trademark "Ninol" are produced by reacting one mole of a fatty acid with 2 mols of diethanolamine. The structure of these compounds has not been established definitely but they are usually considered as nonionic. A variety of products can be made by using various fatty acids and various hydroxy amines. These nonionics are used extensively in detergent formulations as foam stabilizers as well as in many textile and cosmetic applications.

Structure and Surface Activity

Although a vast amount of work has been done on correlating chemical structure with surface activity, there is a lack of general test methods which permit prediction of performance in specific applications. The lowering of surface tension by surfactants does not always correlate with wetting action. Lowering of interfacial tension does not always correlate with emulsification. Dispersing action for one pigment does not correlate with dispersing action for other pigments. In spite of these difficulties it is well to review the results that have been obtained and draw some board generalizations.

A. Solubility: Like other organic compounds, surfactants of higher molecular weight are less soluble than those of lower molecular weight. Solubility increases with temperature and any given surfactant will usually show a maximum efficiency at a certain temperature. Selection of a surfactant for use at a given temperature should be based on tests made at the same temperature. Nonionic surfactants exhibit a phenomenon known as a cloud point. As the temperature of a nonionic solution is raised, a point is reached where the solution becomes cloudy. This cloud-point increases with ethylene oxide content (Figure 13).

B. Surface Tension Lowering or Wetting: Probably the most extensively studied feature of surfactants is their ability to lower the surface tension of water. A variety of methods have been devised to measure this property and the du Noüy ring method is most widely used. Many articles can be found in the literature relating chemical structure of surfactants to their ability to lower the surface tension of water. Surfactant manufacturers often furnish such data in their technical bulletins.

The Draves-Clarkson test¹³ has been used extensively to indicate the wetting power of surfactant solutions. This test measures the time required for a cotton skein to wet out and sink in a dilute surfactant solution. Although Gruntfest, Hager, and Walker¹⁴ have pointed out

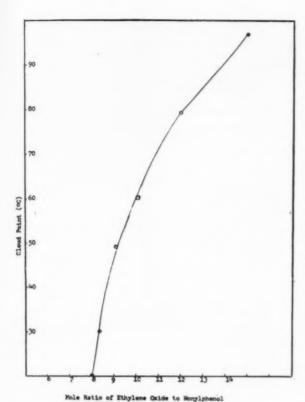


Figure 13-Cloudpoints of nonylphenol ethylene oxide products

some shortcomings of the Draves test, it usually correlates quite well with surface tension and contact angle measurements.

The excellent work by Caryl⁷ on the wetting power of sulfosuccinic acid esters may be cited to illustrate the conclusion that maximum wetting occurs for molecules with a branched chain structure. Thus the 2-ethyl hexyl diester gives a 25 second wetting time at only 0.20 grams/liter while the normal octyl diester requires 0.32 grams/liter.

C. Dispersion: The fact that well dispersed solid particles remain suspended in a liquid is of great importance in paints, varnishes and printing inks. It is first necessary to wet out the solid particles in the liquid medium and then to coat the surface of each particle so that agglomeration does not occur. It is rather difficult to differentiate between surfactants and protective colloids as to the part they play in preventing agglomeration.

Protective colloids may contain ionizing groups, for example carboxymethyl cellulose, or they may be nonionic such as methyl cellulose. One can visualize that protective colloids function by coating finely divided solid particles with a film. This film effectively reduces attractive forces between the solid particles and they remain dispersed.

Anionic or cationic surfactants may be adsorbed on solid particles and provide them with charged surfaces. Repulsion between like charged particles prevents agglomeration. In the case of sulfonic acid surfactants, dispersing action in aqueous systems increases from alkyl to tlkyl benzene to alkyl naphthalene and is greatest for the naphthalene sulfonate condensates. From this and other evidence, it may be concluded that increased aro-

maticity of the surfactant increases the adsorption on solid surfaces.

Nonionic surfactants are quite effective dispersants also, particularly the alkyl phenol ethylene oxide condensates. In this case the hydrophobic groups are adsorbed on the solid surfaces and the polyglycol chains form a film around the particles more or less like protective colloids.

Although these simple concepts are useful for explaining the role of surfactants as dispersing agents, the actual mechanism is believed to be quite complex.

D. Emulsification: Many of the concepts about surfactants as dispersing agents apply equally well to their use as emulsifiers. Hydrophobic groups dissolve in the surface of oil droplets with hydrophilic groups oriented outward into the water phase (conversely for water-inoil emulsions). The most important concept in emulsions is that of an interfacial film between the water phase and oil phase. A strong film prevents coalescence of the dispersed droplets. Charged droplets, like charged solid particles, are stabilized by virtue of repulsion between charged bodies of the same sign.

Nonionic surfactants as a class are quite often superior to anionics or cationics for emulsification. Their ability to form tough interfacial films must be more important than the electrical repulsion factor provided by ionic surfactants. Perhaps the most important structure factor in emulsification is hydrophobic-hydrophilic balance. The ease with which this balance can be altered in nonionics is one reason for their extensive use as emulsifiers.

The technique of making an oil emulsion with triethanolamine oleate by dissolving the oleic acid in oil and the triethanolamine in water can be used with synthetic surfactants. A combination of an oil soluble nonionic and a water soluble nonionic, such as the sorbitol esters and ethylene oxide adducts mentioned earlier, often surpasses a single surfactant. Anionic-nonionic combinations are very effective in many applications. Protective colloids are used for stabilizing emulsion systems.

E. Foam and Detergency: The ability of surfactants to foam has important uses such as ore floation and fire-fighting and is quite important in detergent formulation. Although foaming has been studied scientifically as well as in practical applications, no completely satisfactory explanation of foaming has been developed and little or no correlation with surfactant structure is possible.

Detergency is one of the most important properties of surfactants from a practical standpoint and it is an extremely complex subject. Certainly wetting, dispersing action, and emulsification are all involved in detergency. It is not difficult to measure the relative scouring power of a homologous series of surfactants for soiled cotton and wool (Figure 14), but it is generally recognized that laboratory testing methods do not show which surfactants or formulations are best for all round performance as household detergents.¹⁵

Identification of Surfactants

Accurate identification of surfactants is extremely difficult and requires a variety of analytical tools. It is often possible, however, to obtain a general idea about surfactant structures from simple laboratory tests. As a first step, the manufacturer's technical literature should be studied. The practice of revealing exact structures is growing, at least among the larger manufacturers. Specifications on individual surfactants can be obtained from the manufacturer in many cases and they may furnish analytical procedures upon request.

A clue to the type of structure is often given by a

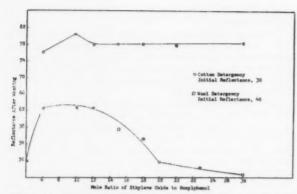


Figure 14—Cotton and wool detergency of nonylphenol ethylene oxide products (0.2% detergent)

product's price or its recommended uses. Products recommended as germicides or corrosion inhibitors are usually cationic. A detergent would be anionic or nonionic. An edible product would be nonionic. A powerful wetting agent is probably anionic whereas a substantive textile softener would be cationic.

Several complications are available which list surfactants by tradename.1-4 For example, McCutcheon lists over 1600 products by tradename and in most cases gives the ionic type, activity, and type of structure. It is interesting to note that about half this group are anionic, one third are nonionic, 11% are cationic and less than 1% are amphoteric.

Preliminary examination of an unknown surfactant would include physical form, color, odor, ash, density, per cent volatile by oven drying, water content by xylene, and solubility in water and common solvents. Portions of a 1% aqueous solution of the unknown should be tested by adding an equal amount of a 1% anionic and also a cationic surfactant. Precipitation immediately or after 24 hours, will indicate the ionic nature of the surfactant whereas no precipitation suggests a nonionic. The following generalities may be used as a guide:

(1) Nonionics are usually oily liquids or low melting waxy solids and would show only a trace of ash. A 1% aqueous solution of a nonionic may exhibit a cloud point at some definite temperature upon heating. If a nonionic is suspected and shows no cloud point, repeat the test in a 3% sodium sulfate solution.

(2) Products in powder form are most apt to be anionic. Products giving very high foam are probably anionic. Anionics are frequently cut with sodium sulfate and will not be soluble in alcohol, xylene, or carbon tetrachloride.

(3) Cationics are often sold as waxy pastes containing water or isopropanol or both. They are substantive to cellulose and will impart a soft, slippery feel to cotton cloth soaked in a dilute aqueous solution.

A qualitative test for nitrogen, sulfur, and chlorine by sodium fusion can be helpful. Most anionics are sulfates or sulfonates and would show positive for sulfur. Most cationics contain nitrogen but nonionics usually contain neither sulfur or nitrogen. Most cationics are chlorides but acetates, sulfates, phosphates, and bromides may be encountered.

Surfactants differ in stability to acid, alkali and salt solutions. Soaps are precipitated by calcium solutions and separate as an oily layer upon acidification. Sulfate esters are usually hydrolyzed by acid solutions but are stable to alkali. Carboxylic esters are saponified in alkaline solutions. Nonionic ethers are stable in both acids and alkalis but are often insoluble in strong solutions of acids, alkalis or salts.

Author's Postscript

Since this article was prepared early in 1956, synthetic detergents have continued their rapid growth and soap sales have declined. In fact, synthetic detergents are now invading the bar market. All synthetic bars as well as soap-synthetic bars are now on the market,

Three recent references may be cited for those interested in surfactant structures and uses. The Chemical Specialties Manufacturers Association sponsored a symposium on ethylene oxide based surface active agents (16). Speel has issued a revised edition of his book on Textile Chemicals and Auxiliaries (17). Schwartz, Perry, and Berch have published a second volume of their comprehensive book on Surface Active Agents (18).

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A New Component of Human Epidermis

A new component of human epidermis, the mucopolysaccharides was described to the New York Chapter of the Society of Cosmetic Chemists October 1 by Dr. Peter Flesch, associate professor of Research Dermatology at the School of Medicine, University of Pennsylvania.

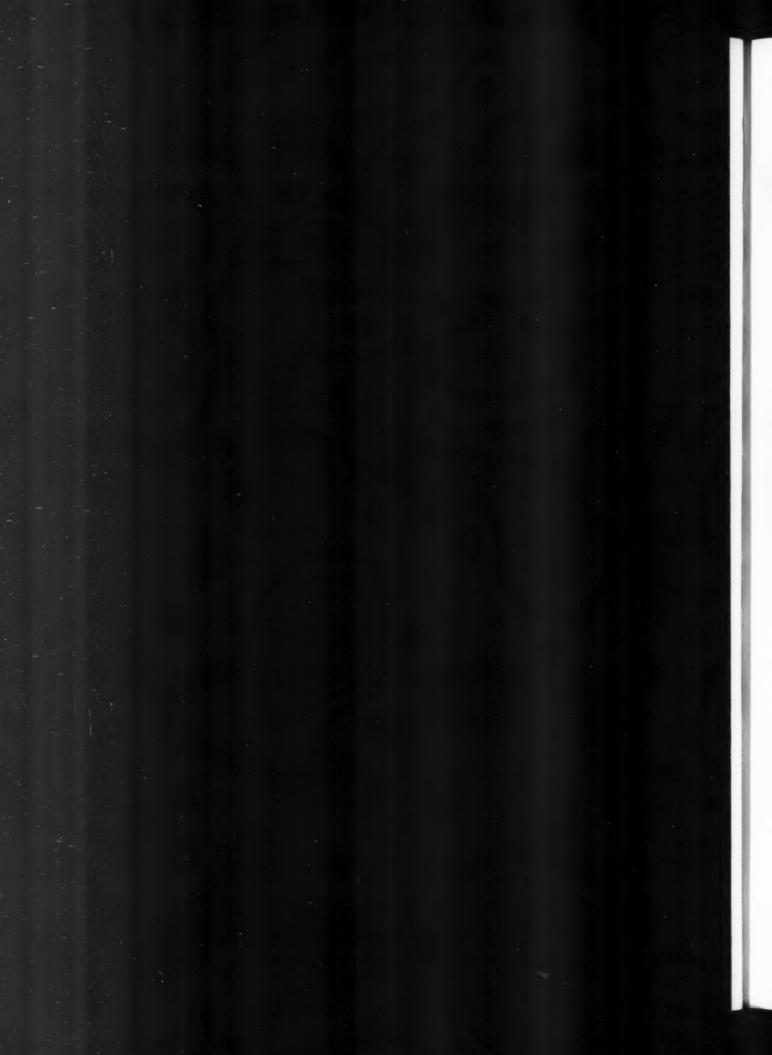
These compounds, recently characterized and studied by Dr. Flesch and other investigators, are non-keratin components of human skin. They are consistently present in a variety of epidermal structures, especially during intense proliferation. The function of these substances in epidermal tissues still is the subject of much speculation. Mucopolysaccharides in other tissues bind water and hold the cells together in a cementing matrix. They may function similarly in the horny layer of human skin. However, there is no conclusive evidence that this is their sole or even principal purpose.

Dr. Flesch said that it is more likely that the mucopolysaccharides enter into the synthesis of keratin, that is, the formation of hair and horny layer. Evidence supporting this view has been obtained from clinical observations of reversible hair loss apparently associated with a number of types of disturbed mucopolysaccharide metabolism in the skin. Although this strongly suggests that mucopolysaccharides are essential for the synthesis of keratin, it is premature to say whether they act as "building stones," "precursors" or "donors of active sulfur."

Aerosol Package Contest

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By W. B. STANTON*

Warren B. Stanton obtained his bachelor's degree in chemistry from Princeton University in 1949 and joined Wyandotte Chemicals Corp. in 1950. He is now assistant manager of surfactant sales with Wyandotte Chemicals Corp.



BLOCK POLYMER SURFACTANTS

All surfactants contain a water-insoluble portion called the hydrophobe, and a water-soluble part which is the hydrophile. Most nonionics employ an ethylene oxide condensate for the hydrophile and for the hydrophobe, a readily available, water-insoluble material such as an alkyl phenol or fatty alcohol, among others. The ethylene oxide addition to the hydrophobe can be controlled, but only a limited number of hydrophobes are economically available in each class. For instance, there is no inexpensive homologous series of alkyl phenols or fatty alcohols. However, a new class of nonionic surfactants was conceived when chemists at Wyandotte Chemicals Corp. discovered that polypropylene glycol with a molecular weight of 900 or more was ideally suited as a surfactant hydrophobe.

Because high molecular weight polypropylene glycol is a polymer, the subsequent condensation of ethylene oxide onto each end of the base polymer results in the formation of block polymer surfactants. A series of them were first introduced commercially in 1950 under the Pluronic** trademark. These polypropylene glycol polymeric hydrophobes can be made to almost any desired length. Since both the hydrophobe and the hydrophile are polymers, the total molecular weight and the hydrophobe-hydrophile balance can be readily controlled. Therefore, it is possible to "tailor make" the surfactant as desired.

The first block polymer surfactants offered commercially were made by condensing propylene oxide onto propylene glycol until a polymer of the desired length was obtained. The reaction was continued using ethylene oxide which was added onto each end of the polyoxypropylene chain to produce a surfactant having two hydrophilic ends and a hydrophobic central portion. The simplified molecular structure is shown in Figure 1. Because the hydrophobic and hydrophilic portions of the molecule could both be varied, it was possible to plot the molecular structure on a graph by plotting the hydrophobe against the hydrophile.

(SECOND DIGIT ! 0 2101 - 2500 1501-1800 1201 - 1500 1001 - 1200 801-1000 POLYOXYETHYLENE POLYOXYPROPYLENE POLYOXYETHYLENE HO(CH2-CH2-0), (CH-CH2-0) (CH2- CH2-0), H CH3 TREND OF PROPERTIES ACROSS GRID MAN ECLE AR WEIGHT SUBFACE ACTIVITY CARRON SOR, REMOVAL ENCELLENT

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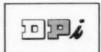
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Figure I is such a graph. It is called the Pluronic Grid, in which six hydrophobe molecular weight ranges are arbitrarily chosen and listed on the vertical axis. The percentage of polyoxyethylene in the total molecule is shown on the horizontal axis. Bracketed numbers along the verticle axis identify the molecular weight range of the hydrophobes and are also the first digits in the numbers of the final surfactant. The numbers along the horizontal axis indicate the percentage of ethylene oxide which has been incorporated into the final molecule and are the second digits of the surfactant's number. To complete the nomenclature system, a letter, L. P. or F, is added to indicate a liquid, paste or flakable solid material. Thus, a block-polymer surfactant in this series having a hydrophobic base weight of about 1750 and containing about 40% polyoxyethylene would be found to be a liquid and would be called L64.

A systematic technique for evaluating the properties of block-polymer surfactants was a natural outcome of the graphic representation of molecular structure. It was soon realized that small incremental changes in the molecular structure or the ratio of hydrophobe to hydrophile produced incremental changes in the properties and these changes could be drawn on the grid as a trend. The testing of two or three members of the series usually indicates the trend for any particular property, and by following this trend, the best member of the series can be selected without evaluating the entire group of available products. This simplified method for evaluating surfactants is unique to the block-polymer type.

Several common property trends are shown beneath the grid in Figure I. By following the trend line on the grid, it is often possible to select a single surfactant having the desired balance of properties for the given application, but when a single satisfactory product is not available, blending members from different parts of the grid often gives the desired results. For instance, the addition of about 10% Pluronic L61 will effectively reduce the foam of the other members of the series. None of the block-polymer surfactants of the type shown in Figure 1 are high foaming, but those members towards the left side of the grid are almost non-foaming. However, the dispersing and suspending properties of the series are greatest among the high molecular weight members which are in the upper right quadrant of the grid. It is interesting to note that the higher molecular weight products are solids which are available in flake form. The cloud point, primarily a function of the hydrophobic-hydrophilic ratio, increases with increasing oxyethylene content.

Surfactant toxicity is an important consideration for cosmetic chemists. While complete toxicity information for Pluronic surfactants is not yet available, preliminary information indicates the toxicity is very low.

Several Pluronic surfactants have been tested for oral toxicity. The LD_{50} of L44, L62 and L64 for rats was found to be 5 gm/kilo, but the LD_{50} of F68 for mice was greater than 15 gm/kilo and it was not physically possible to administer larger doses. Chronic feeding studies were made which indicated that after six months of daily doses of 0.1 and 0.05 g of F68 per kilogram of body weight, no gross symptoms of toxicity were noted in dogs, nor were symptoms of toxicity in evidence after feeding rats 3% and 5% F68 for six months.

Eye irritation tests conducted with L44, L62 and L64 using the Draize Test (6), indicated irritation was negligible at common use concentrations. (7) Although Pluronic F68 was not studied in this manner, 5% and 10% solutions, applied to the conjunctival sac of rabbits, produced no detectable irritation.

Various skin sensitivity tests have been conducted as described below:

- 1. Skin sensitivity studies (8) employing the challenge test technique with Pluronic F68 were made on dogs, rabbits, guinea pigs and man. F68 was made into a 75% paste and applied every other day for ten applications. Fourteen days after the last application, the paste was again applied. There was no evidence of skin irritation or of hypersensitivity reaction.
- The application of a 50% solution of F68 to skin wounds on the abdomen of rabbits did not significantly influence healing time as compared with control wounds.
- 3. Patch tests with L44, L62 and L64 on humans in the laboratories of Wyandotte Chemicals Corporation indicated no evidence of irritation of sensitizing effect. Preliminary work was done by the prophetic test method (9) using 5% and 85% solutions of the above surfactants in a group of 12 men and 12 women. No irritation was observed. Thirteen days later similar patches were placed in the same order on 19 of the 24 subjects. Again there was no evidence of irritation.

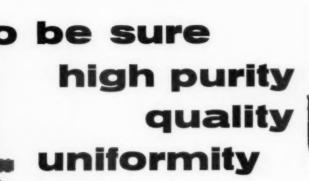
Because shampoos are of interest to many cosmetic chemists, the grease removal from hair was studied in the Wyandotte laboratories using essentially the same method as that proposed by Barnett and Powers (10). Of the polymeric surfactants tested, those with the more hydrophobic character were most effective. Maximum grease removal occurred when the molecular weight of the hydrophobe was about 1200 to 1800 and when the molecule contained 10% to 20% ethylene oxide units. The data obtained plus that previously reported by Barnett and Powers are listed below.

GREASE REMOVAL OF SURFACTANTS

0.25% Active	Agent)
Composition	Grease Removal, %
Pluronic L50	49.1
Pluronic L51	93.7
Pluronic L54	58.1
Pluronic L62	83.9
Pluronic L64	74.5
Pluronic F68	39.8
Sodium alkyl sulfate	98.2
Alkylaryl sulfonate	92.2
Alkylaryl ethers	92.3, 69.1, 56.8
Potassium coconut soap	90.3
Fatty ether	57.2
Fatty acid ester	53.0
Water	17.0
Cationics	-8.5 to -12.7
Commercial Shampoos	-0.8 to -91.0

It is interesting to note that the data for the Pluronic surfactants can be plotted as trends on the grid in Figure I. The block-polymer surfactants available at the present time have good cleaning properties on hair, but their low foam makes them generally unsuitable as the primary surfactant in shampoos, although they are used as lime soap disperants in soap-based shampoos.

The versatility of polymeric surfactants is not limited only to those of the general structure shown on Figure I. Other block polymers can be made based upon the same concept of the polyoxypropylene hydrophobe by condensing propylene oxide onto other suitable nuclei such as glycerin, ethylene diamine or a monohydric alcohol. Polyoxypropylene chains will form at each point in the nucleus containing a labile hydrogen atom so the degree of branching can be controlled by selecting the proper







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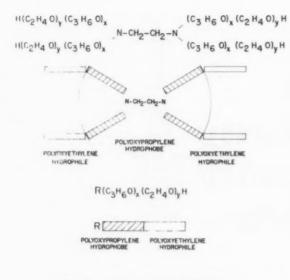
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TYPICAL BLOCK POLYMER SURFACTANTS

Figure II

starting molecule. Two typical block polymer surfactants are shown in Figure II. Of these, the material based upon ethylene diamine and having four branches is commercially available under the name Tetronic* at several hydrophobe-hydrophile ratios. The molecular weight in this series can be as great as 27,000 or as low as 1,000. The four terminal hydroxyl groups and the two tertiary amine groups make this structure interesting as a chemical intermediate, but in general, the properties are quite similar to those of the Pluronic series. Blockpolymers employing a monofunctional nucleus as a starting material are more conventional in that one end of

the molecule is the hydrophobe and the other is the hydrophile. Toxicity studies have not been initiated for the Tetronic series, so they are recommended for investigational use only at this time.

SUMMARY

Block-polymer surfactants, formed by the sequential addition of propylene oxide and ethylene oxide onto a suitable nucleus such as propylene glycol or ethylene diamine, can be prepared in various molecular weights and almost any desired hydrophobe-hydrophile ratio. The wide range of molecular structure and resulting properties are unique to the polymeric surfactants.

The molecular structure can be plotted on a graph and the properties of the surfactant series indicated as a trend on the same graph. This technique is a time-saving procedure making it unnecessary to evaluate the entire series when investigating any particular property. The polymeric surfactants developed to date are available in liquid, paste or flake form. The foaming properties in water vary from almost nil to moderate, and the toxicity, in general, is extremely low.

Block-polymer surfactants can be used by the cosmetic industry where their unique properties such as low foam, lack of taste (for high molecular weight grades) or dispersing properties can be utilized.

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NEW YORK CHAPTER OF S.C.C. TO HONOR NATIONAL PRESIDENT

As has been its custom since its founding, the New York Chapter of the Society of Cosmetic Chemists has invited the incumbent President of the national Society to be the guest-speaker at the closing meeting of the year. On November 5, 1958, James H. Baker, president of the Society of Cosmetic Chemists, will be honored by the New York Chapter at a dinner-meeting.

Besides discussing a few matters pertinent to the Society, Mr. Baker will talk about that "Unwanted Cosmetic Ingredient—Bacteria." His talk will be of a practical nature, citing a few instances where bacteria played havoc with some cosmetic products; how these products were affected; the nature of the culprits and, in some instances, the solution to the problem. He will also relate some work showing the deleterious effect of nonionics on the para-hydroxy benzoic acid esters. A bacteriological procedure for determining the effectiveness of preservatives in cosmetic products will be given, together with interpretations and precautions. This talk will be more practical than theoretical and should be of extreme interest to every cosmetic chemist because all are subject to the problem of preserving their products.

Mr. Baker, although born in the United States, lived and received a large part of his education in Canada. After graduating from Acadia University, Nova Scotia, in 1929, Mr. Baker took his Masters Degree in Chemistry at Columbia University.

In 1931, he organized the consulting and development laboratory known as Gar-Baker Laboratories, Inc. During these past 27 years, he has been associated with the development of many cosmetic items, the preservation of which often became a vexing problem both as to the solution and the time required to be sure of the solution.

Mr. Baker, a charter member of the Society, has been most active as Program Chairman, inaugurating the "Special Award" and by serving on various other committees.

^{*}Registered trademark of Wyandotte Chemicals Corp.

AMPHOLYTIC Detergents





Donald L. Andersen is a project leader in the Chemical Research Department of the General Mills Central Research Laboratories, where he has been employed for nine years, joining General Mills shortly after receiving his B.S. degree in chemistry from Northwestern University. His responsibilities include product and process development and applications research on fatty nitrogen derivatives, especially detergents and corrosion inhibitors. He has published several papers on ampholytic detergents.

D. L. ANDERSEN*

Comparatively unknown but a few years ago, ampholytic surface active agents now have become a significant factor in the specialty detergent field. Ampholytes exhibit a unique combination of anionic and cationic functionality. This inherent versatility, and their compatibility with cationic surface active or germicidal agents offers a wide range of applicability, especially in the cosmetic, textile and metal fabricating industries.

Chemical Properties

Surfactants in general can be defined as compounds containing hydrophobic and hydrophylic groups, and exhibiting marked reduction of the surface energy of a solvent (usually water) when present in low concentration. Ampholytic surface active agents can be characterized further as containing, in addition to a hydrophobic group (usually a long straight-chain hydrocarbon), at least one cationic hydrophylic group (usually an amino or quaternary nitrogen), and at least one anionic hydrophylic group (usually a carboxylic acid, sulfate, ester, or sulfonic acid group). These cationic and anionic hydrophylic groups can be equal in number (balanced ampholytes), or one or the other many be in excess (unbalanced ampholytes).

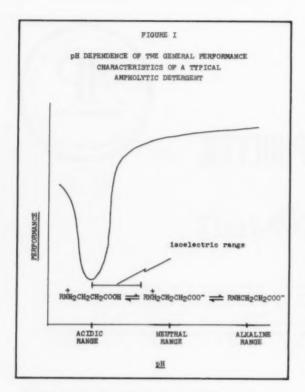
Electrochemically, amphoteric (a term used interchangeably with ampholytic) surfactants are positively or negatively charged, or essentially neutral depending on the pH of the solution. In alkaline media, an amphoteric will be characterized by essentially anionic properties, and in acidic media, it will exhibit essentially cationic properties. At or near neutrality, although electrochemically nonionic, the ampholytic

detergent is unique in its combination of anionic, cationic and nonionic properties. Since most cosmetic formulations are essentially neutral, the unusual polyfunctionality of the amphoteric in this pH range offers extensive applicability to problems in this field.

Performance Characteristics

Versatility is the key to the applicability of the amphoterics to a wide range of problems. This versatility is derived from three major factors: variation of the hydrophobic portion of the molecule (the various fatty acid based materials, for example); variation in the degree of balance (monoamino-monocarboxylic, monoamino-dicarboxylic, polyamino-sulfated, etc.); and control of pH. Taken separately or in combination, these various controls offer the possibility of selecting from a family of products, a specific product to solve a given problem. In applications requiring carefully controlled surface active properties, the amphoterics offer a degree of control impossible with almost any other surfactant. In shampoo applications, it is possible to obtain cleansing of the hair and scalp without excessive defatting. In textile applications, it is possible to obtain controlled wetting or rewetting, or to affect removal of the ampholytic adjunct by simply altering pH.

The surface active behavior of a given ampholyte is highly pH dependent. To define performance characteristics for any product or family of products, conditions of acidity or alkalinity also must be defined. A typical plot of a given performance function versus pH passes through a minimum (occasionally a maximum) at or near the isoelectric pH (range of minimum solubility or the pH at which the ionic charges are



internally compensated). See FIGURE I, which represents the actual curve for Ross Miles foam volume versus pH of a typical balanced ampholytic, N-lauryl aminopropionate.

Ampholytic detergents exhibit, to more or less varying degrees (depending on the hydrophobic portion, the degree of balance, and the particular salt or ionic form), the normal spectrum of surface active properties. However, certain performance properties of the ampholytics are of special interest. These include: substantivity to the skin and hair and to fibers, bacteristatic properties, low toxicity, hard water tolerance, compatibility with cationics, hydrotropic (solubilizing) properties, emulsification, and controlled foam, wetting and detergency.

It has been postulated that the properties of substantivity, low toxicity, and bacteristasis are essentially related to one another, and are derived from the similarity of the amphoterism of proteinaceous substances to that of ampholytic surfactants. As a result, bacteristatic and substantive properties of most ampholytics appear to be generally most effective in neutral or even somewhat acidic solutions.

Ampholytics offer cationic compatibility over a very wide pH range. Similarly, good hard water tolerance (calcium and magnesium ion compatibility) is observed over a wide pH range. Properties such as foam, wetting, and detergency are more or less dependent on pH, and it is in this pH dependence that control of these functions is possible.

Specialized applications such as emulsification and solubilization represent areas in which the versatility of the amphoteric can be utilized and is required in the fullest. Classically, the polyfunctionality of the amphoteric molecule ideally fulfills the prerequisite that "two emulsifiers are better than one." Similarly, the versatility of the amphoterics makes possible a "synthesis" of chemical and physical properties needed to solubilize a given substance in a given system.

Known and Suggested Uses

The economics of ampholytic detergents as a general class suggests their use in more or less specialty applications. These products are generally derived from other than the least expensive raw materials, and are arrived at through relatively complex processes. Hence, it is doubtful that the ampholytics can compete directly with the much cheaper petroleum derived surfactants. However, in the areas of specialization and in the solving of specific problems in surface active chemistry, there is little doubt that the amphoterics will gain increasing acceptance.

Amphoteric detergents have ben indicated as adjuncts to soap and/or other synthetics in the formulation of partially or wholly synthetic detergent bar soaps. The properties of substantivity, bacteristasis, and hard water tolerance offer many advantages.

Shampoo formulations containing one of the higher foaming ampholytes as a major ingredient or as an additive will offer a whole range of new or improved performance characteristics. Difficultly soluble germicides can be brought into solution with ampholytic solubilizers. Formulations with relatively large quantities of quaternaries are possible because of the cationic compatibility of ampholytes.

Textile applications include: dispersing, emulsifying, wetting, wool scouring, wool fulling, resin finishing, and softening.

Amphoterics find use in the metal fabricating industry as additives to plating baths, as specialty cleaners and degreasers, and as drawing lubricants.

Emulsion polymerization, latex emulsions, freezethaw stabilizers for emulsions, agricultural emulsions, etc., are suggested as applications for the unique properties of ampholytics in general.

Miscellaneous, but nonetheless important applications include: detergent sanitizers, household liquid detergents, alkaline cleaners, corrosion inhibitors (industrial and in aerosol formulations), cosmetic emulsifiers, etc.

Availability

Both in the United States and Europe, the number of commercially available amphoteric surfactants has increased greatly in the last few years. TABLE I attempts to summarize these products, but no claim can be made for absolute completeness, the picture changes almost daily.

TABLE I
TABULATION OF CURRENTLY COMMERCIALLY AVAILABLE

An	IPHOTERIC SURFACE ACTIVE	AGENIS
TRADE NAME	GENERAL STRUCTURE	COMPANY
United States		
Product BCO	cetyl betaine	duPont
Product BDO	long chain betaine	duPont
Soromine AT	complex fatty amido compound	Antara
Antaron FC-34	complex fatty amido compound	Antara
Janusol	fatty esters containing both amino and sulfated groups	Synthetic Chemicals, Inc.
Berapon S-60	complex fatty amido compound	Berkshire Color and Chemical Co.
Miranols	complex imidazole carboxylic acids	Miranol Chemical Co.
Deriphat 170	N-lauryl aminopropionate	General Mills, Inc.
Deriphat 160	N-lauryl iminodipropionate	General Mills, Inc.
Deriphat 154	N-tallow iminodipropionate	General Mills, Inc.
Deriphat 151	N-coco aminopropionate	General Mills, Inc.
Syntergent 130-W	modified ethylene oxide condensate	Nopco Chemical Co.
Armeen SZ	N-coco aminobutyrate	Armour Chemical Co.
Duponol XL	pseudo amphoteric	duPont
Europe		
Amfaid L	-	Norman Evans & Rais, Ltd., England
Desil	Amino sulfonic acid	P. R. Masek Ltd. England
Tego	fatty polyaminoethyl glycine	Th. Goldschmidt A.G. Germany
Amphionic	probably a fatty amino acid	Glovers (Chemicals) Ltd., England



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Musk Ketone 100%
Musk Xylol 100%
Musk Tibetene®
Ambrettolide L.G
Thibetolide
Versalide®

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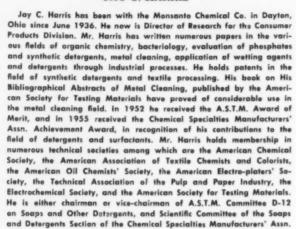
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JAY C. HARRIS*





Alkylbenzene Sulfonates

Cosmetic. **Formulations**

The greatest single economic stabilizing force in the surfactant industry has been substitution of alkylbenzene sulfonate for the fats and oils previously required for detergent manufacture. Climatic, seasonal, economic demand, or other factors which previously controlled soap costs have been substituted by alklybenzene and sulfuric acid, the constituents of which (olefin, benzene, and sulfur) unlike the natural products, are well-stabilized materials.

The condensation of an olefin, generally propylene tetramer, with benzene followed by sulfonation, has become a straightforward process. Alkylbenzene (AB) can be sulfonated either by the AB manufacturer (there are five large-tonnage suppliers), or in the customer's plant on a batch or continuous scale commensurate with demand. As contrasted with the large expensive equipment for AB manufacture, equipment for the sulfonation step can be as complicated or as simple as the customer requires. Units for oleum sulfonation (with concomitant free acid which generally ends up as sodium sulfate) or sulfur trioxide sulfonation (product essentially saltfree) have been announced.

Alkylbenzene sulfonates (hereafter called ABS, and signifying the sodium salt) are available from several basic manufacturers, and many custom suppliers. Table 1 lists the ABS or other salts as active ingredient contents more generally useful for cosmetic preparations. All such products are listed in McCutcheon's 1958 list (Soap, Jan. thru April 1958).

In spite of their apparent points of superiority, surfactants have not achieved the acceptance of soaps in cosmetic preparations. Possible reasons are: (1) they have not been available in a variety of salts, or (2)

preparative requirements have not permitted the manipulation in formulation of fatty acids (or oils) or their variety when combined with ethanolamines. If these are the main reasons, they should no longer fully

A new development which should increase usage of ABS is the availability of alkylbenzene sulfonic acids which the customer may neutralize or manipulate in the formulation as he requires. This should change many manufacturing procedures and should permit the research man to utilize more fully this important surfactant. Shown in Table 2 are several such acids.

Properties of ABS which should be considered in cosmetic formulation work are solubility; resistance to metallic and hard water ions; feel on the skin; and possibility of allergic effect.

ABS compounds of specified solubility can be achieved by selection of the neutralizing base used for the salt. Sodium and potassium salts are the least water soluble, but both are readily soluble in alcohol. The ammonium or ethanolamine salts are very soluble, and also exhibit increased viscosity characteristics. Magnesium salts are quite soluble, but calcium, aluminum and other metal salts are relatively insoluble. Solubility in water increases as the alkyl carbon chain length is decreased, Cs being most soluble, C_{10} less soluble, C_{12} soluble, C_{14} relatively less soluble.

While ABS salts are stable toward acid, the solubility of the salt takes the same order as the alkyl chain length, the C₈ being most soluble under these conditions. Acid solutions of metallic salts are more stable than their neutral" or normal counterparts, and the lower alkyl carbon chain length benzene sulfonates are most useful in such media. Salting out of the ABS salts occurs in the same order of carbon chain length.

^{*}Monsanto Chemical Co., Research and Engineering Division, Dayton, Ohio

TABLE 1
ALKYLBENZENE SULFONATES

	Na	me	Manufacturer	C Chain Length or Type	Physical Form	Activ
	onco A	AS-50-M AS-60	Continental Chem.Co.	=	Liquid-Ammonium Salt Liquid-Triethanol-	50
					amine Salt	60
C	onoco	C-50	Continental Oil Co.	12-polypropylene	Paste	45
)etergei		Pilot California Co.	_	Flake	40
U		nt D-40	Oronite Chem. Co.	12-polypropylene	Granular	40
	"	D-60	"	"	"	56
D)eterger	nt Slurry	"	"	Slurry	42
K	Creelon	4D	Wyandotte Chem. Corp.	_	Flake	40
	**	8D	"	_	99	85
N	lacconol	DB	National Aniline Div			
			Allied Chem. & Dye Corp.		Bead	40
	11	HG	"	_	Flake	60
	**	NRSF	"		"	92
	**	Z	"		"	85
	"	60S	"		Liquid-Organic Salt	60
P	ilot AL		Pilot California Co.	_	Liquid-Ammonium Salt	00
	1100 241	-40	r not Camornia Co.			40
	" HI	0-90	29		in Alcohol	
	" SP.		"	-	Flake	92
	" TS		"		Paste	56
	15	-00	**	APPAREL I	Liquid-Triethanol-	-
a		N 1	M		amine Salt	60
2	antome	rse No. 1	Monsanto Chem. Co.	12-propylene	Flake or Powder	40
	111	85	"			85
	99	S	"	10	Liquid	30
		SX		10	"	30
	79	3	"	12-propylene	Paste	65
	**	E	"	8-propylene	Flake	70
Si	iponate	DS10	American Alcolac Corp.	_	Powder	98
	ole-fona		Sole Chem. Corp.	_	Flake	92
Se	orapon	SF-78	Antara Chem. Div			
			Gen. Aniline & Film Corp.	Flake —	Flake	85
St	tepan I	S-60	Stepan Chem. Co.	_	Liquid	50
SI	ulframi	n AB40	Ultra Chem. Works, Inc.	-	Flake or Powder	40
	77	AB Conc.	"	_	Powder	80-85
	11	KE	"	10	Liquid	25
T	repolate		Treplow Products, Inc.	10	Flake	95
-	19	T-60	"		Liquid-Triethanol-	20
					amine Salt	60
	00	YLA	n		Liquid-Amine Salt	95
171	ltrawet		Atlantic-Refining Co.	Polypropylene-	Liquid-Alline Sait	30
O	trawet	20	Adamic Tenning Co.	Intermediate	Flake	85
	"	K	"		riake	99
		V		Polypropylene-	"	OF
	"	2000	"	High		85
	**	30DS	"	Polypropylene	Liquid	25.5
		60L	**	**	Liquid-Organic Salt	60

TABLE 2
ALKYLBENZENE SULFONIC ACIDS

Name	Manufacturer	Form	% Active
Conoco Sulfonic Acid 400	Continental Oil Co.	Liquid	88 and 98
Monsanto DDBSA	Monsanto Chemical Co.	Liquid	86
Pilot ABS-99	Pilot California Co.	**	98
Sole-fonate 98	Sole Chemical Corp.	**	98
Sulfonic Acid	Jacques Wolf & Co.	Paste	85
Sulframin Sulfonic Acid	Ultra Chemical Works, Inc.	Slurry	84
Trepolate Acid	Treplow Prods.	Liquid	97 .

The bacteriostatic effectiveness of ABS has been described in several papers. It is generally believed that the surfactant is preferentially adsorbed by the protein of the bacteria, forming a relatively stable complex simultaneously inhibiting further bacterial growth. This characteristic of adsorption by proteinaceous surfaces is evidenced also by its adsorption on the skin, causing a stickiness. That "tanning" of the skin surface is the probable mechanism involved is suggested by the work of Lundsted who showed that protein (from feathers) combined in regular proportions with ABS. However, this involved physical adsorption, since the ABS could be removed by continued leaching or rinsing.

The stickiness of ABS was recognized many years

The stickiness of ABS was recognized many years ago, and the method used to overcome it was to combine with ABS a compatible material of greater attraction for the protein, but free from apparent stickiness. A new

proposed solution to this problem involves use of watersoluble, long chain, linear polymers of ethylene oxide (Polyoxes); the mechanism of stickiness prevention is not indicated, unless it be their viscous character in solutions.

With the foregoing properties in mind, the several products in which ABS has been most successful will be indicated.

Bubble Bath Basic ingredients for a dry product are:

1) Bubbling material

2) Water softener

3) Carrier for perfume4) Perfume oil and color

The bubbling ingredient in a large proportion of all dry preparations is the sodium salt of alkylbenzene sulfonate, generally in the least expensive dry form, frequently the 40% active product.

The water softener most generally used is sodium sesquicarbonate, desirable for its free-flowing, bulky, uniform appearance and low cost. Alternatives, many of which are superior softeners, are disodium phosphate, trisodium phosphate, tetrasodium pyrophosphate, tripolyphosphate, borax, sodium carbonate or bicarbonate. Frequently, mixtures of these are used to control density, appearance, and cost.

In many cases, a carrier or absorbent for the perfume is used, serving also to control flow and caking, and provide an advertising feature. Examples of these are starch, milk powder, buttermilk powder, bran, oatmeal or bentonite. Small percentages of tricalcium phosphate prevent caking.

Choice of *perfume oil* and *color* are quite important to a product of this type for consumer acceptance and appeal. Perfume can prove a major cost factor, though probably well worth any increased expense.

Process of preparation is simple: Drum, ribbon, or cone blenders can be used. In some cases, master batches of the carrier containing the perfume and color ingredients can provide better control than by individual batch blending.

Formula 1	
ABS (40%)	50
Sodium Sesquicarbonate	37
Bentonite	10
Perfume	1
Tricalcium Phosphate	2

Liquid preparations frequently require mutual solvents to maintain clarity for low temperature stability and frequently because the perfume content may be relatively high. The alkylbenzene sulfonates chosen should be liquid, suggesting the use of lower alkyl chain lengths such as C_8 or C_{10} and/or selection of ammonium or alkanolamine salts. Preparation may be improved by dispersing the perfume oil in a concentrate of alkylbenzene sulfonate and any mutual solvent used.

Shampoos. Advantages of synthetic agents over soap are their neutrality, resistance to hard water, free rinsing, and for ABS, its actual adsorption by the hair to condition it for setting and waving. Because surfactants are such good emulsifiers and cleaners, they may tend to dry the hair and scalp if used without added conditioner: This is overcome by the addition of emollients.

The shampoo may be formulated as a paste, gel, cream, or liquid, depending upon the ABS salt and the other ingredients. This permits a wide choice of packaging.

Cream shampoos containing ABS can be prepared (DeNavarre, American Perfumer, March 1947), using as opacifiers and thickeners: polyol stearates, soap, specmaceti, cetyl alcohol and many others. Additional materials are gums, bentonite or colloidal magnesium aluminum silicate. An example of this type is:

	%
ABS (60-85% active)	16.6
Tergitol 7	33.3
Bentonite	7.4
Cellosize WS 100	5.7
Water, perfume oil, color	q.s.

Ingredients to provide sales points are exemplified by powdered egg, dandruff preventives, lanolin, bacteriostats, deodorant ingredients.

Liquid Shampoo Formula

C 10 ABS	12.5
C 12 ABS	12.5
Sulfonated Oil	5.0
Carbitol	2.5

Perfume and color are added as desired, the balance comprising water.

Conditioning agents to be used with above:

	6
Carbowax 1500	- 4
Carbowax 4000	4
G 1441	5
Diglycol laurate	1
Diglycol oleate	1
Ethyl oleate	1
Ocenol	1

Toilet Bar. The use of surfactants in milled toilet bars is increasing. Improved lather, solubility, and rinsing characteristics, and compatibility with deodorant materials may be the controlling factors in this change.

The use of ABS in such formulations is indicated on a cost basis if for no other reason, of which there are several already apparent. As with most cosmetic formulations, and even milled soap bars, combinations of surfactants are of value to achieve specific effects; ABS may be only one of several used. Here again, the apparent stickiness of the product on the skin could be a deterrent unless means are taken to circumvent it. Use of small percentages of metallic soaps help, combination with other emollient surfactants has been used, and a recent suggestion has been the use of high molecular weight ethylene oxide polymer (Polyox) as lubricant.

A bar stock formula suggested (Union Carbide Chemicals Co.) is representative:

Material	Se
ABS (65 to 85% active)	41
Sodium lauryl sulfate	15
8:20 Tallow-coco soap	30
Calcium stearate	6
Titanium dioxide	1.5
Polyox WSR-35 or 205	2.0
Water, perfume	q.s

SUMMARY

The cosmetic usage of alkylbenzene sulfonates seems to have been restricted largely to bubble bath, shampoo and toilet soap manufacture. Increased usage of alkylbenzenes and of their sulfonates can be expected as "packaged" sulfonation plants increase. A sulfonation process giving an essentially salt-free product permits choice of salt type and should expand usage where sulfate salts are deleterious. Recent availability of free sulfonic acids promises increased usage for those not equipped for the sulfonation step. The sulfonic acid offers manipulative variation not heretofore possible and should result in completion to the established fatty acid-alkali systems.



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sarcosine	sarcosine	sarcosine	sarcosine	sarcosine

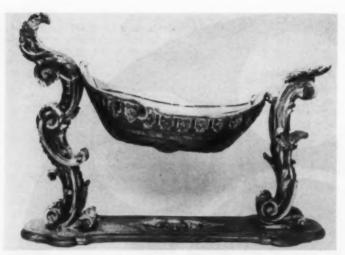
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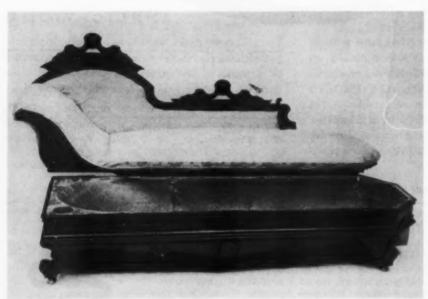
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FRENCH LOUIS XVI GILDED CRADLE TUB: Circa 1754-1793. Probably a French courtesan once bathed in this regal, elaborately ornamented, carved wood cradle tub; the frame and tub are completely gilded with 14 carat gold leaf. The cradle, with removable metal basin insert, is suspended about $3\frac{1}{2}$ feet high between two rococce columns set en a decorative platform. The tub tilts slightly downward so the bother could nestle in the basin and extend her legs out onto the top of the column. There was no drain arrangement, but the basin could be unhooked and emptied. This lush period of history is appropriately symbolized by the lushness of the bath. This was also the era of the elaborate toiletts—perfumes, unquents, pomades, cosmetics—and some regalty even added red rose petals to their baths for beauty. People liked to be amused in the tub by musicians, and they frequently dined and wined while bathing. Photo courtesy of Cleanliness Bureau.

Elaborate and Practical Forerunners of Our Modern Bathtubs

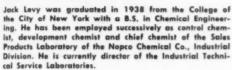




ENGLISH REGENCY SHOWER: Circa 1810. This 12-foot high tole shower, which probably graced an English manor house, was considered to be the most unusual bathing apparatus of its day. Made of metal, painted to look like bamboo, this shower consists of a basin with drain on the bottom and a hidden tank at the top—joined by poles about 10 feet long. A pump arrangement on the lower basin forces water up to the top basin through ane hollow pole and then down over the bather's head—with the same water reused time and time again. Small hinges around the top hold a form of shower curtain and the bather probably wore a tall conical hat made from an oiled material—forefather of the modern shower cap. This was the era of the dandy, when men were as fussy as the ladies about their toilettes. After showering, the men would perfume themselves and choose their clothes for the day—an exceedingly difficult task. Photo courtesy of Cleanliness

VICTORIAN SOFA TUB: Circa 1880 to 1890. This American-style Victorian tub doubled as both a proper living room sofa and as a bathtub. The entire top of the sofa could be removed, revealing a full length metal tub complete with a niche for soap. Some styles were more ornate than this one, and many were overstuffed, black leather upholstered versions. This one, made of carved and scrolled walnut, is upholstered in gold brocade and has one curved armrest a la Madame Recamier. Some of these practical, convenient, comfortable, portable, complete, and economical sofatubs were advertised as "the common sense invention of the age." This type tub had to be bailed out, and a gutta percha "apron" was placed around it to protect the carpet from splashes. The living room tub came about because most houses were not equipped with specific bathrooms. Today, the Germans are manufacturing a new triple threat Victorian type sofa-tub that unfolds to reveal a bed, and lifts up to reveal tub -the only new twist is a drain connection. Photo courtesy of Cleanliness Bureau.







Next to soaps, sulfated oils are the oldest synthetic surface active agents. Developed originally as dye-bath assistants for the level dying of cotton fabrics, these products of the reaction between sulfuric acid and a vegetable oil were known as sulfonated oils. While today it's recognized that this is a misnomer and that technically these materials are sulfated products, the original name has become so strongly entrenched that it is still widely used and frequently both terms are used interchangeably.

The raw materials for the manufacture of sulfated oils are the naturally occurring liquid fats such as olive oil, peanut oil, castor oil, etc. or the liquid waxes such as sperm oil, and sulfuric acid.

In order for an oil to be capable of being sulfated it must contain in its structure either a reactive double bond as in most of the common liquid fats or a hydroxyl group as in hydrogenated castor oil or both as in castor oil. While tallow, which has an iodine value of about 40 (iodine value is a measure of the number of double bonds in a compound) can be sulfated, hydrogenated oils because the iodine value has been reduced to below 5 cannot; nor can coconut oil which has an iodine value of about 8. On the other hand, hydrogenated castor oil still contains a hydroxyl group and can be sulfated.

The sulfation process is essentially a simple one. Sulfuric acid is added slowly to a suitable oil, usually with cooling to prevent excessive darkening and polymerization. After the acid has been added and the mass mixed for a suitable period of time to assure uniformity and time for the reaction to take place, it is washed with water or a salt solution to remove the excess of acid and it is then neutralized with alkali.

The characteristics of the finished sulfated oil depend on the following facts:

- 1. The nature of the oil which was treated.
- 2. The quantity of sulfuric acid with which the oil was treated—in general the greater the quantity of acid,



Julgated



the higher the SO3 content and the more "soluble" the finished oil.

- 3. The time and temperature at which the reaction was carried out.
- The temperature and duration of the "wash"-during the "washing" procedure hydrolysis of the glyceride occurs and the extent of hydrolysis determines the emulsifying and blending characteristics of the finished oil.
- The quantity and kind of alkali used in neutralization of the "washed" oil.

The sulfated oils most widely used in the cosmetic industry are those derived from olive oil or similar high quality vegetable oils and those made from castor oil. These are used as bases for non-lathering shampoos, as solubilizers for essential oils, as leveling agents for hairdyes to assure even coloring, as emulsifiers or auxiliary emulsifiers in many types of cosmetic emulsions and for the formulation of soap free detergents for individuals and situations where the use of soap is contraintroduced.

Sulfated oils have many properties which make them valuable as components of cosmetic formulations.

- 1. They are liquids even at a low water content. Sulfated oils at 75-80% activity are common and it is even possible to obtain commercial products with lower water content. All of these are fluid at room temperature and easily handled.
- They are outstanding emulsifiers for essential oils, vegetable oils, mineral oils and waxes. They can be formulated to blend clearly with these materials and, depending upon the relative quantities of sulfated oil and raw oil yield products which give water solutions which range from brilliantly clear through opalescent to milky.
- 3. They are emollient in nature and leave the skin or hair soft and pliable after application. This characteristic is quite the opposite of that of many other detergents which frequently leave the skin dry. This characteristic is evident even when the application is made as a very dilute solution such as might occur when a sulfated oil is used as the basis

for a bath oil. In spite of the relatively small amount of sulfated oil added to the average bath as the solubilizer for the perfume oils, its effect is noticeable in the feel of the skin after the bath and the apparent "softness" (probably really a slight oiliness) of the bath water.

4. They are moderately resistant to hard water and do not form insoluble soaps with calcium or magnesium. When used in shampoo formulations, therefore, they do not leave a film of insoluble soaps on the hair with the corresponding dull, lifeless ap-

pearance

They are usually manufactured to have a neutral or slightly acid pH. Since the pH of normal skin is in this range, they tend to be less irritating than many other detergents which have an alkaline pH.

In spite of all of these desirable qualities, sulfated oils have never achieved the prominence which these properties would seem to warrant. In the field of shampoos particularly real success has not been achieved primarily because sulfated oils do not produce a lather. The consuming public has come to associate effective cleansing action with copious lather and, as a result, do not consider nonfoamy detergents as being capable of performing as well as the foamy types. This prejudice exists in spite of evidence that foam is not necessarily connected with detersive or cleansing action.

Detergents and shampoos based on sulfated oils are also relatively expensive if only because of the high active content which they usually contain. Most products of this type are at least 50% active while other shampoos usually contain only 15-20% active ingredients with the

balance in both cases being water.

Because of these two factors, lack of foam and high cost, there has been a gradual decline in the sales of sulfated oils for shampoo and detergent uses with the nonionics, sulfated fatty alcohols and diethanolamine condensates taking over more and more of the market. In spite of this, there is a persistent feeling among people active in the industry that sulfated oils have a definite place and that their special qualities of blandness, neutral pH and emollient action ensure them a continuing market.

It is difficult to give formulas for compounding detergents and shampoos based on sulfated oils because of the differences in blending properties in those from different manufacturers. However one supplier suggests the following formulations for a non-lathering shampoo—

Sulfated vegetable oil 45.0 37.5 40.0 35.0 80-90 sec white mineral oil 15.0 12.5 15.0 10.0 Water 40.0 50.0 45.0 55.0

These are prepared by placing all of the components in an open kettle and mixing cold until clear and uniform. After blending in a suitable perfume and color, if desired, the products are ready for packaging.

A satisfactory bath oil may be prepared according to the following formula:

90-95% sulfated castor oil 5-10% perfume

Here, too, color may be added and the product may be packaged without further treatment. Further information on formulations using sulfated oils may be obtained from various manufacturers.

Some of the more prominent manufacturers of sulfated oils are:

E. F. Drew and Company—Boonton, New Jersey

Hart Products Corporation—New York City

E. F. Houghton Company—Philadelphia, Pennsylvania Nopco Chemical Company—Harrison, New Jersey

Onyx Oil and Chemical Company—Jersey City, New Jersey

Developing a Selling Formula

HAZEL BISHOP*

Intensive scientific research in an area where wild exaggeration exists is discouraged because the consumer seeks the sensational product and dramatic cure in cosmetics as in medicine. A superior cosmetic created by chemical research might still fall short of advertising claims.

Science can make more effective hand and face creams, nail preparations, and perfumes. But unless the manufacturer is assured that the products will be purchased, he cannot afford to finance their creation and marketing. Thus it is as vital to establish the companion selling formula as it is to create the superior chemical formula.

Development of a selling formula requires an awareness of the peculiar nature of cosmetic products which are intended for cleansing, beautifying, promoting attractiveness or altering the appearance. Inherent in the superior cosmetic must be the promise to fulfill more satisfactorily not only a visible or physical function but also the deep-seated urge to be attractive. . . .

Since the merit of the chemical composition of a cosmetic cannot be perceived at a glance, the potential consumer is naturally more captivated by the greater promise of the promotion department's imagination. Such a condition discourages real chemical research. Why spend money and effort to create a superior product if the chemical objective to be sought would fall short of what already is claimed to be an actuality?

Since it is axiomatic that a manufacturer can stay in business only so long as he can sell his product at a profit, he may find it necessary to restrict himself to the types of research more likely to pay off, such as seeking to make a current product more cheaply, searching for a more convenient or esthetic packaging, or a visual or sensory improvement, or creating a chemical product to which he can validly apply an exciting, unexploited claim

to attract the potential consumer.

Of all of the above, the last mentioned research problem offers perhaps the greatest thrill to the creator as well as the greatest reward, along with the greatest challenge. The gamble is gigantic because such a product usually falls into the class where effectiveness of consumer appeal is greatly influenced by upbringing and past advertising. As an example, the stymying influence of the 'French Myth' in the perfume field has caused the dollar volume of perfume sales to remain virtually static in the face of increased population and devaluation of the dollar.

There is a fifth type of research project—the one which appears to assume prime importance for many manufacturers—that is, the search for the 'magic ingredient...' The development of a magic ingredient which possesses scientific soundness is likely to involve vast expenditure beyond the scope—or possibilities—of a cosmetic manufacturer. This type of research had best be left to the basic chemical house.

On the other hand, the 'magic' promised by a type of substance such as that derived from an animal, insect, or flower—if really valid—would probably put it into the drug category and thus make it unsuitable for incor-

porating into a cosmetic.

Whichever the type, the cost per pound of such a substance would probably be so great that only a token amount could feasibly be incorporated into the product formula, thereby achieving promotional rather than functional value.

*Abstract from an address before the Chemical Marketing Division, American Chemical Society, Sept. 12, 1958.





CLYCLOIMIDINIUM **AMPHOTERICS**



HANS S. MANNHEIMER*

Hans S. Mannheimer is president of the Miranol Chemical Co. of which he was one of the founders in 1940. The company was of which he was one of the founders in 1940. The company was incorporated in 1943. He is the inventor of the compounds his company manufactures and is the holder of 39 American patents and a considerable number of foreign patents. Mr. Mannheimer was educated at the Technische-Hochschule in Aachen, Germany where he received his B.S. degree.

A mphoteric Surface Active Agents as a class appeared to be virtually unknown in spite of the fact that they postdated the anionic compounds by only a few years and are actually older than the nonionics. The earliest patent on record in the United States is Platz & Holsten, Appl. 1934, U. S. Patent #2,097,864, Nov. 1937, an I. G. Farben development. The first patent of a product developed in this country, Downing & Johnson, Appl. 1935, U. S. Patent #2,129,264, Sept. 1938, a DuPont development. While in the interim years quite a number of other new Amphoteric Surfactants were developed according to the patent literature, not a single one of these products was actually on the market in 1950. If this should appear strange in view of the present day interest, let us examine Amphoterics a little closer and the reason for this may become more apparent.

In every other class of surface active agents general behavior within the group is reasonably predictable if compared to such radical differences as between anionics, cationics and nonionics (among each other). This, however, is not true in regard to Amphoterics. This group embraces compounds which in their behavior have nothing more in common than the designation. This designation means only that these compounds have in their structure one or more cationic and one or more anionic groupings. If one or the other type of groups is stronger than the other, which is usually the case in most Amphoteric compounds, because the relative strength of a group is easily influenced (MannheimerNitrogene Compound Symposium-C.S.M.A., May 1958), we are dealing with compounds with principally cationic or predominantly anionic properties. Such unbalanced Amphoterics may have none or only limited compatibility with anionic or cationic surfactants depending on their orientation (Freeze et al American Perfumer "Shampoo Uses" March 1956), Only the balanced Amphoterics in which the cationic and the anionic groups are of exactly equal strength are compatible with all other surface active agents in all proportions and although these balanced compounds react more anionically in the alkaline range and more cationically in the acid range their total compatibility remains unimpaired.

This factor plus others which we shall examine shows clearly why the balanced Amphoteric is the most desirable compound in the cosmetic industry. There are no anionically oriented Amphoterics on the market today. Since these products offer no advantage over anionic surfactants, the reason for this is clear. There are a number of cationically oriented in addition to the only two balanced Amphoterics, U. S. Patent #2,528,378, see formula below and U.S. Patent #2,773.068

*R represents the fatty acid radical and, therefore, changes according to the derivative.

The cationically oriented product is naturally just like the true cationic surfactant a poor detergent and is, therefore, not well suited for shampoos or any other cosmetic product involving cleaning, such as cleansing creams. In contrast to this the balanced surfactant behaves in the neutral range like a nonionic with the exception that it is a good foamer, as are many of the Amphoterics. In the alkaline range (above pH7) it behaves more like an anionic surfactant without, however, completely assuming the character of these products. In either case the detergency is good, rendering the product eminently suitable for the formulation of shampoos and other products requiring cleaning ability.

Amphoterics tend to plate in monomolecular layers thereby imparting hair conditioning and combability to shampoos. Since the balanced Amphoteric, being a good detergent, can be used by itself or with anionics in all proportions, this conditioning effect can be superb without reduction in foaming capacity as is incurred by the use of the so called conditioning agents.

The cationically oriented Amphoteric being not well suited for shampoos by itself for lack of detergency is only suitable in mixture with anionics in ratios of 1-6. or 1-4 with the more expensive triethanolamine salts (Freeze et al). At this low ratio, however, the hair conditioning effect is not very high.

It is, therefore, no real surprise that the interest in Amphoterics in the cosmetic industry did not begin until the advent of the balanced compounds; all others being products which have long been known dating in part back to the Platz & Holsten patent with the difference that new and simpler methods have been invented which, however, still yield the compounds known for many vears.

One of the first commercial cosmetic products in which Amphoteric surfactants were used were medicated shampoos containing quaternary ammonium salt germicides. Anionic surfactants being incompatible, nonionics were in use when it was found that these combinations caused opacification of the cornea, quaternaries being preferentially employed over the chlorinated plenol types because of their considerably broader spectrum. While the poor foaming properties of such combinations had been taken in stride, there being no other choice, the injurious properties of the combination made a formula change imperative. Amphoteric surfactants fitted the requirements perfectly. Since their compatibility with quaternary ammonium germicides was an established fact it only remained to test possibly injurious effects. Such test showed that these combinations passed the Draize Test (Draize, Woodard and Calvery) with a very low score, provided the quantity of quaternary germicides was adequate but not excessive. Such combinations in contrast to the older ones were found to be excellent foamers and imparted good combability and manageability to the hair.

Amphoterics have been used with great success in the formulation of soap shampoos. The foam of MIRANOL SM CONC. or MIRANOL C2M CONC. is wholly compatible with that of soap, so that no loss occurs in mixtures as with anionics. They reduce the cloud point of potassium soaps to practically freezing level and render clear solutions at thawing. These compounds have good lime dispersion properties but that in itself is not unusual. Most surfactants have this quality. However, the MIRANOL Amphoterics do not only disperse but actually

dissolve lime soaps rendering clear solutions in high dilutions, as for instance in rinsing after shampooing. This startling property together with the fact that they do not in the least affect the inimitable "feel" of a soap shampco, makes it possible to obtain a shampoo product which possesses all the advantageous properties of a synthetic detergent without losing those qualities for which soap shampoos have been so well liked. The use of a triethanolamine soap in such combinations is neither required nor desirable because the triethanolamine plus the amine content of the Amphoteric creates a cationic balance which, as pointed out above, creates poor performance. A typical formulation follows:

25% Potassium Coconut Soap 40%

15% MIRANOL SM CONC. or MIRANOL C2M CONC

Hexylene Glycol (not required if soap contains glycerol)

5892 Water

100%

Perfume to suit

A small quantity of amine condensate may be added if increased viscosity is desired.

Amphoteric surface active agents also filled a need in the hair rinse field. Cationic surfactants were employed here successfully but it was found that they tended to impart a greasy feel to the hair if used in excess, that they were not completely removed in subsequent shampooings and, therefore, were prone to build up on the hair and gradually caused the formation of a dull gray film, which in part also consisted of insoluble precipitate between cationic rinse and anionic shampoos.

Combinations of Amphoterics with cationics changed the physical structure of the deposit on the hair causing softness without greasiness and imparted washability to the rinse. Because of the greater solubility of the Amphoteric, a less firm bond between the rinse and the negatively charged hair formed and provided a solubilizing bridge between cationic and anionic, eliminating the film build up. An additional advantage was realized in the following respect. Most hair rinses are creams. Cationics tend to thin out in the acid pH range in which most rinses are employed resulting in thin watery products requiring additional products to build up the body of the compounds. Such body builders are not necessarily beneficial for the best performance of the product. Amphoterics do not undergo major physical changes through pH adjustments, particularly not those of stearic derivation. It is, therefore, possible to formulate hair rinses with utmost simplicity. e.g. 5% MIRAMINE (Cationic stearic derivative,

tertiary amine)

MIRANOL DM (Stearic Derivative, Type I) 10%

85% Water

100%

Perfume to suit

Perhaps the most important invention in the cosmetic field were the non-irritating and non-eye stinging surfactants. Since they are based on Amphoteric surfactants they are properly treated here. A typical representative of these products described in 29 U.S. Patents is shown

U.S. Patent #22,781,354



Exploring the Secrets of Nature

Applying new scientific knowledge to develop synthetic aromatics hitherto unknown Re-creating, synthetically, precious natural distillates and extracts

These are problems successfully mastered by our research chemists and perfumers.

Experiences thus gained inspire to further DRAGOCO ACHIEVEMENTS

*BULGARYOL synthetic Bulgarian rose oil

NEROLYOL synthetic Neroli oil big. pet.

BIGARADIA perfect reproduction of "Absolu de Fleurs d'Oranger».



DRAGOCO INC. NEW YORK

For many years now it has been maintained, especially by interested parties, that 1% of all humans are allergic to soap or synthetic detergents. This claim can hardly be substantiated. Barail, using the intradermal single injection method on rabbits, compared Miranol 2MCA Modified with an olive oil castile soap. The castile soap produced a definite reaction (2++) while the Miranol 2MCA Modified showed no irritation.

A typical formulation of a non-irritating and non-eye stinging shampoo follows:

30% MIRANOL 2MCA MODIFIED

2% Hexylene Glycol

1% Ninol AA62 Extra (or equivalent)

Atlas G 7596J (or equivalent) 1%

66% Water

100%

Perfume to suit

Even in ordinary mixtures of Amphoterics and anionics some salt formation may take place although of lower order. Sufficient salt is formed if such compounds are mixed at a ratio of 2-1 or 1-1 to practically eilminate all irritation to skin and eye, Although eye sting under these circumstances will be attenuated it will not be completely eliminated in such mixtures. Particularly in the case of MIRANOL C2M CONC. combinations, irritation is completely eliminated due to the fact that the product itself is completely free from irritation. It can be readily seen that such combinations offer numerous advantages over the ordinary shampoo formulation. Skin and eye irritation can be depressed to a level far below that of the least irritating standard such as Olive Oil Castile Shampoo. The commonly used sulfated alcohols, are even more irritating. Combability and manageability are imparted to the hair without loss of foaming properties usually encountered by the use of so called conditioning agents. Cost of such formulations is only very slightly above those of the usual sulfated alcohol based shampoos. Formulations are crystal clear with very low cloud point and are exceptional foamers even on first application.

15% MIRANOL C2M CONC.

Lauryl Sulfate Sodium Salt (Sipon LS or 15% equivalent)

Hexylene Glycol

1 % Atlas G 7596 J

67% Water

100%

Perfume to suit

Additional viscosity can be obtained by employment of a small quantity of a "Super Amide." It is to be noted that the selection of any substances to be used in this formulation as well as in the formula based on MIRA-NOL 2 MCA MODIFIED must be selected with great care in order not to destroy or materially reduce the non-irritational qualities. Some perfumes, triethanolamine salts, soaps, free fatty acids, esters and all freely ionizing compounds can very quickly raise the irritation

Another application where the non-irritation to skin and eyes of MIRANOL C2M CONC. finds a fertile field is in the preparation of foaming cleansing creams. These products which are used on sensitive facial skin and which can easily be rubbed into the eyes should be completely free from all irritation. Where with shampoos much of the facial contact can be accidental, these products are deliberately rubbed into the skin. Their removal after cleansing is often rather sketchy and even if the face is washed after their use, the cream base is likely to hinder their complete removal. It would stand to reason that detergents showing a + + reaction or higher in the intradermal injection test should not be used. Formulations with MIRANOL C2M CONC. are safe and inexpensive. A Liquid Cream Formulation follows:

10% MIRANOL C2N CONC.

Ethoxylated Stearyl or Cetyl Alcohol 5%

85%

100%

Perfume to suit

Non-irritating Amphoteric salts are used for the preparation of paper coated waterless facial and hand cleaners

MIRANOL MSA MODIFIED

U.S. Patent #2,781,357, equally non-irritating and noneye stinging as MIRANOL 2MCA MODIFIED is preferred for this because of lower viscosity stages than the latter and a more readily release from paper.

Liquid Bubble Bath preparations are products where MIRANOL Amphoterics are used with advantage. Their excellent foam stability combined with their previously pointed out compatibility with soap results into foam with excellent stability by the use of soap in the tub. In addition their lime soap solubilizing power results in even cleaner bath tubs than is customary with other surfactants.

MIRANOL L2M-SF CONC. 20-40%

(Linoleic derivative Type II)

1- 2% Perfume

79-58% Water

100%

The range in the formulation is shown above to indicate variations depending on the desired product quality. While most perfumes are soluble in MIRANOL L2M-SF CONC. solvents (e.g. Hexylene Glycol) in the range of 5-10% may be added where necessary without impairing product quality.

A new application is currently under investigation, namely the production of tightly knit foams as a vehicle for dispensing suncreams, sunburn relief, insect repellents and others in readily dispersable and nonirritating form in aerosols.

The foregoing clearly shows that the balanced Amphoterics have found their way into every major surfactant

application in the cosmetic field.

Opportunity for Cosmetic Sales

Just reviewing the sales figures over the past ten years shows that toiletry volume has almost doubled and the rate of increase goes up year by year. When you start looking at the future there are some extremely optimistic signs. One of them could be summed up in the song "Thank Heaven for Little Girls." Little girls get bigger every day add the words "Thank Heaven for Little Boys." Take those little girls and little boys. By 1965 there will be about 24 million teen-agers. When you realize that the over-all population will probably increase about 24% during the next 15 years it certainly is of more than passing interest to all of us that the increase of teen-agers will be a 71% boost or three times greater than the over-all population—and I don't have to tell you the importance of the teen-ager in moving cosmetics across the country: girls using lipsick earlier than ever before-boys getting more particular every day about hair dressing to be used in the house. They won't accept what Pop happens to bring home. What a splendid opportunity lies ahead for all of us .- Richard Lockman.

POLYHYDRIC ALCOHOL **ESTERS** FOR COSMETIC USE





DR. S. I. KREPS AND J. STARKMAN*



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Fatty acid esters of a wide variety of polyhydric alcohols are employed in cosmetic and pharmaceutical formulation. This type of material comprises a major division of nonionic surfactants which are used as emulsifiers, wetting, dispersing and suspending agents,

opacifiers, thickeners, anti-foaming agents, plasticizers, and lubricants.

Classification of the polyhydric alcohol esters may be made on the basis of either component. Manufacturers' catalogs and specifications indicate that nearly all the fatty acids are employed, including among the most common the laurates, stearates, oleates and ricinoleates. Often coconut fatty acid esters are marketed as laurates, while other grades of the same materials are made with high purity lauric acid. A variety of ester grades are produced with any one polyol, the quality and utility depending upon the grade of fatty acid employed. Esters of other naturally occurring fatty acid mixtures are supplied using materials such as corn, linseed, cottonseed, sunflower, perilla, soybean and palm fatty acids, but these esters have not found any great acceptance in cosmetics.

The polyols used offer an equally wide choice. Ethylene and propylene glycols, diethylene glycol, glycerol and higher polyols are components of cosmetic grade surfactants. Among the more common higher polyols are polyethylene glycols, polypropylene glycols and sorbitol. Esters based on sugar have recently been

introduced on an experimental basis. The nature of the final product is profoundly affected

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by the method of preparation employed. The polyoxyalkylene esters may be produced by reaction of olefin oxides with the appropriate fatty acids. This results primarily in the formation of monoesters. The same esters may be prepared by direct esterification of the fatty acids with polyalkylene glycols, but in this case equilibrium mixtures of mono and diesters are obtained. The nature of the mixture depends upon the functionality of the polyol, the molecular ratio of the polyol and fatty acid reactants employed, and the degree of completion of the reaction. A third method of manufacture involves ester interchange between the polyol and a simple ester of the fatty acid. Here also equilibrium mixtures are obtained, but these equilibria may differ considerably from those characteristic of direct esterification. Accordingly, many materials sold under the same chemical designation are not necessarily equivalent in function.

Manufacturers' specifications for any given ester indicate the wide range of grades which may exist in each case. For example, glyceryl monostearate (GMS) is offered as a distilled grade of high purity, as socalled GMS "pure" containing only about 50% monoester, as self-emulsifying GMS and as acid-stabilized GMS. Acid values specified for these materials may range from a maximum of 2 to a value of 30 or even higher. Saponification values, melting ranges, iodine values, free glycerine and monostearate content also cover a wide range. The comparative utility of a particular product with a particular specification cannot generally be determined only from the specification.

Many suppliers list but a limited number of these

esters in their catalogs out of the literally hundreds of compositions which are possible. They are usually prepared, however, to manufacture any ester to specifications desired by the purchaser. Table 1 presents

TABLE 1

Typical Ester Types	Representative Trade Names (Suppliers)		
Glyceryl Monostearate, Distilled	Myverol (5)		
Glyceryl Monostearate, Pure, Self-Emulsifying, and Acid-stabilized	Arlacel 161 (1) Abracol GMS (2) Aldo 28, 33 (7) Cerasynt S, SE, 1000 D (10) Emcol MSC (6) Kessco Wax (9) Glyceryl Monostearate C (3) Tegin 515, Tegacid (8)		
Ethylene Glycol Laurates, Stearates Oleates, etc.	Emcol ETS (6) Cerasynt M, MN (10) S-147 (7)		
Polyethylene Glycol Laurates, Stearates, Oleates, etc.	S-1000 Series (7) Nonex Series (11) Emulsynt Series (10) Cerasynt Series (10)		
Higher Polyol Laurates Stearates Oleates, etc.	Span series (1) Arlacel 83 (1) Crill Series (4) Emulsynts (10)		

Representative Trade Names of Nonionic Ester Surfactants.
(1) Atlas Powder Co. (2) A. Boake, Roberts and Co., Ltd. (3) Coigate-Palmolive Co. (4) Croda, Ltd. (5) Distillation Products Industries, Division Eastman Kodak Co. (6) Emulsol Chemical Division, Witco Chemical Co. (7) Glyco Products Company, Inc. (8) Goldachmidt Chemical Corp. (9) Kessler Chemical Corporation, Inc. (10) Van Dyk & Company, Inc. (11) Gemec Chemical Company (England).

a summary of representative ester types, some of the trade names under which they are offered, and the manufacturers. This is not intended to be an exhaustive list; complete lists have been published by deNavarre^{(1)*} and McCutcheon⁽²⁾. Many of the materials offered are not specifically identified chemically. Such materials, manufacturers' specialties, are often proprietary rather than pure chemical compositions which are specifically designed for one or more particular functions not performed as well by the simple chemicals, or by simple mixtures of chemicals.

Another method of classification of the esters depends upon the functions they serve. Many attempts have been made to correlate function with molecular structure of the surfactant. The more highly water soluble esters are used as solubilizing and wetting agents. These are most often the monoesters which have a relatively large polyol portion in the molecule. As the size of the polyol decreases, the oil solubility of the esters increases, and rather than wetting, dispersing and solubilizing functions, the esters become primarily effective emulsifiers.

The nature of the emulsion formed, whether O/W or W/O, is partly dependent upon the emulsifier. Thus, as the polyol portion of the molecule decreases, or as the amount of diester and higher esters in the composition increase, the emulsifiers tend to change from O/W to W/O types. However, the nature of the emulsion depends to a large extent not only on the nature and amount of the emulsifier but

also upon the ratio of water and oil phases, upon the presence or absence of electrolytes, and upon the procedure used to prepare the emulsion. Auxiliary emulsifiers, if present, will greatly influence the nature of the emulsion formed.

deNavarre^(a) briefly discusses the effect of number of ethylene oxide units on the functional properties of nonionics. Table 2 correlates this discussion with the polyethylene glycols available for preparation of surfactants by direct esterification:

TABLE 2

Size of PEG Fraction	Approximate No. of ETO Units	Major Field of Function of Corresponding Monopalmitates
Ethylene glycol Diethylene glycol Triethylene glycol		Oil Soluble Not dispersible in water W/O emulsifiers
PEG 200	4	Water dispersible, $W/O \\$ emulsifier
PEG 300	6	Easily water dispersible, O/W emulsifier
PEG 400	9-10	Water soluble, maximum wetting and surface active activity
PEG 1000	20	Very water soluble. Good emulsifier for polar com- pounds, not for hydro- carbons
PEG 2000	40	Solubilizer

The identity of the fatty acid also affects the characteristics of the emulsifier. This is a major effect in the case of emulsifiers with relatively small polyol chains. As the size of the polyol moiety increases, the effect of changes in the fatty acid becomes progressively less. In general, the trend from W/O to O/W types is in the order: oleate, stearate, laurate. Thus the polyols of oleic acid such as Arlacel 83, Emulsynts 1048 and 1049, or Crill 16 will form predominantly W/O emulsions even when the oil/water ratio is very low. However, the type of emulsions formed by laurate and stearate polyols is more dependent upon the oil/water ratios in the formulation.

The effect of reactant ratios may be demonstrated by the differences between specific stearates. Distilled glyceryl monostearate (Myverol) is predominantly a W/O emulsifier while ordinary glyceryl monostearate (Tegin M, Cerasynt S, Aldo 33, Abracol GMS) can produce either type of emulsion. The self-emulsifying grades of GMS usually contain small amounts of soap. The addition of this auxiliary emulsifier in materials such as Tegin, Cerasynt SE and Aldo 28 results in predominantly O/W emulsifiers.

Nonionic esters may be used in preparations encompassing a wide range of conditions. They are compatible with both anionic and cationic surfactants. However, when the preparation is strongly alkaline, the esters are subject to saponification which will destroy their chemical identity and effectiveness.

At the acid end of the pH scale, the surfactant esters are more stable and can be used in the range usually encountered in cosmetic preparations. For use in preparations such as astringent and deodorant creams and lotions which are strongly acid and contain high

^{*}Superscripts refer to Bibliography citations, q.v.

concentrations of electrolytes, acid-stabilized emulsifiers are available. Materials of this type are offered under such trade names as Tegacid, Cerasynt 1000 D, and Kessco Wax. An example of an antiperspirant lotion using this type of emulsifier is given in Table 3.

TABLE 3

	Suntan* Lotion O/W(3)	Hair Groom W/O(1)	Hand Lotion O/W(2)	Anti- perspirar Roll-ball Lotion (3)
Cetyl Alcohol	1	_	1	
Mineral Oil Isopropyl	2	33.5	1	_
Linoleate (3)	1	_	_	
Anhydrous	_	3	1	1
Ceraphyl 31 (3	3)	-		2
Petrolatum	_	5	_	_
Stearic Acid	3	-	-	_
Oleic Acid			2	-
Beeswax Amerchol	*****	2	-	_
L-101 (1)		5	_	-
Cerasynt 1000 D (3)	_	-	_	3
Tegin P (2)	_		6	-
Sorbitan				
Sesquioleate	_	3	-	
Cerasynt WM	3) 7	_	_	_
Water	74.3	47.75	83	44
Propylene Glyc	col 6	_	-	3
Glycerine	_	-	5	-
Urea	2	_	-	_
Triethanolamin	ne 1	-	1	_
Borax	-	0.5	Name o	
Veegum (4)	_	0.25	-	_
Aluminum Chlo hydrol, 50%	or-			
solution (5)	-	-	-	40
Escalol 206 (3	3) 2.7	-		-
Preservative Perfume	q.s.	q.s. q.s.	q.s.	q.s.

Polyol Esters in Cosmetic Formulation

Numbers in parentheses indicable sources of formulations and raw mate-

(1) American Cholesterol Products, Inc.
(2) Goldschmidt Chemical Corp.
(3) Van Dyk and Co., Inc.
(4) R. T. Vanderbilt Co., Inc.
(5) The Reheis Company.

Many nonionic surfactants decrease the effectiveness of germicides when the ratio of nonionic/germicide is above a certain level characteristic for each combination. Wedderburn(4) in a recent study declares that sorbic acid, formaldehyde, benzoic acid, phenylmercuric nitrate and acetate appear to be the best germicides for preservation of preparations containing the nonionic surfactants. deNavarre(5.6) has also published recent work on this subject.

No rules can be presented concerning the types of nonionic esters used in specific classes of cosmetic products: there are nearly as many modes of formulation as there are formulators. The following outline indicates some of the more common types of polyol ester surfactants as revealed in published formulae.

In general, nearly all the esters are employed as emulsifiers and emollients in emollient creams and lotions. Cold creams based on borax-beeswax often employ GMS as an auxiliary emulsifier.

Cleansing creams employ GMS, diethylene glycol stearates, and sorbitan esters as stabilizers, thickeners and auxiliary emulsifiers. Cleansing lotions are formulated with diethylene glycol laurates, glyceryl stearates and laurates. Stearates of ethylene, propylene and polyethylene glycols are emulsifiers and thickeners in hand lotions. A typical formulation is shown in Table 3. For medicated creams and lotions: hormones, vitamins, antibiotics, W/O, nonionic emulsifiers are often preferred since these surfactants are chemically inert. An example of a suntan lotion is offered in Table 3, this is a O/W type. A W/O type hair grooming preparation is also shown.

In clear shampoos, materials such as glyceryl monolaurate, PEG 400 or 600 distearates are used as hair conditioners. In cream shampoos, hair conditioners may also include GMS and diethylene glycol stearate. As opacifiers, ethylene glycol and glycerol mono and distearates are used.

Lipstick formulations call for polyethylene glycol and propylene glycol monolaurates as solvents and coupling agents for bromo acids. The higher polyethylene glycol 400 stearate are used as suspending and dispersing agents for pigments in make-up formulations.

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Marketing Set-Up Changed

Our whole marketing set-up-in many instances the basic concept of the toilet goods business has undergone radical changes, Richard Lockman moderator of the Merchandising Panel at the recent Toilet Goods Assn. convention, reports.

"With explosive growth of the teen-age market and the now obvious fact that today's woman equates the pursuit of beauty with the pursuit of happiness, all I can say is Well, fasten your seat belts-because we're really going to start to go.

"I think we can all agree there will be more and more basic research, more and more of the zealous search for that extra plus to put into a product, not to mention the new product itself.

"As to new products I think all of us in talking with many retailers and even some manufacturers have found that the acceptance of this new-products trend is sometimes a passive one. Often there has been great reluctance to accept the fact that the never-ending stream of new and improved products is the life blood of our business.

"Every year we see further evidence that the cosmetic business follows more ardently than ever before the philosophy behind the fashion industry-new styles, new ideas. A recent analysis of toilet goods sales shows that 40% of the volume done today in drug stores comes from products not available five years ago. And it is interesting to keep in mind that every new product introduced by a competitor eventually winds up as added volume for you, added profit for you. A successful new product is bound to spark numerous variations, imitations—if I am allowed to use the word-to suit the myriad tastes of women. We all know too how new products stimulate interest among consumers-often reclaiming customers who dropped out of the market entirely because they were dissatisfied with an item.'



ALKYLOLAMIDES IN COSMETICS





W. J. LENNON AND I. M. ROSENBAUM

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l. M. Rosenbaum is a member of the sales staff of Geigy Industrial Chemicals. He joined Geigy in 1957 after serving as an officer in the U.S.A.F. He received his B.A. Degree from Gettysburg College in 1954. Both authors have done work in the field of Optical Brighteners, Ultraviolet Light Absorbers, Chelating Agents, Bacteriostats and Surface Active Agents.

An estimated 4,000,000 lbs, of alkylolamides are used annually by the cosmetic industry. This class of nonionic compounds includes fatty acid condensates of diethanolamine, monoethanolamine and isopropanolamine.

These amides are generally used in conjunction with anionic, nonionic or cationic surface active agents as viscosity and detergency improvers, foam stabilizers, lime soap dispersants, emulsifying or solubilizing agents. The alkylolamides may also be used in the absence of other surfactants as in bromate neutralizers as opacifiers and thickeners, in hair rinses as softeners, in hair dyes as combination carrier and bodying agents.

The alkylolamide condensates most familiar to the cosmetic chemist are derived, according to a process developed in 1937, by Dr. Wolf Kritchevsky, by the condensation of 2 moles of diethanolamine with 1 mole of fatty acid at 150-170°C. (2:1 type amides). These condensates are water soluble products when derived from capric, coconut, or lauric acids; water dispersible if derived from oleic, myristic, or stearic. These 2:1 type condensates, which have been of primary commercial interest for the last 20 years, are not single chemical entities but actually a complex mixture of at least six or seven different constituents according to a number of papers published to date. 2.3,4,5,6 The following compounds and levels indicated are believed to be present in typical 2:1 type alkylolamides:

TABLE I CHEMICAL COMPOSITION OF ALKYLOLAMIDES

1)	Fatty Amide	RCON(CH2CH2OH)2	50%
2)	Amine Ester	HN-CH-COOR	10%

CH₂CH₂OH

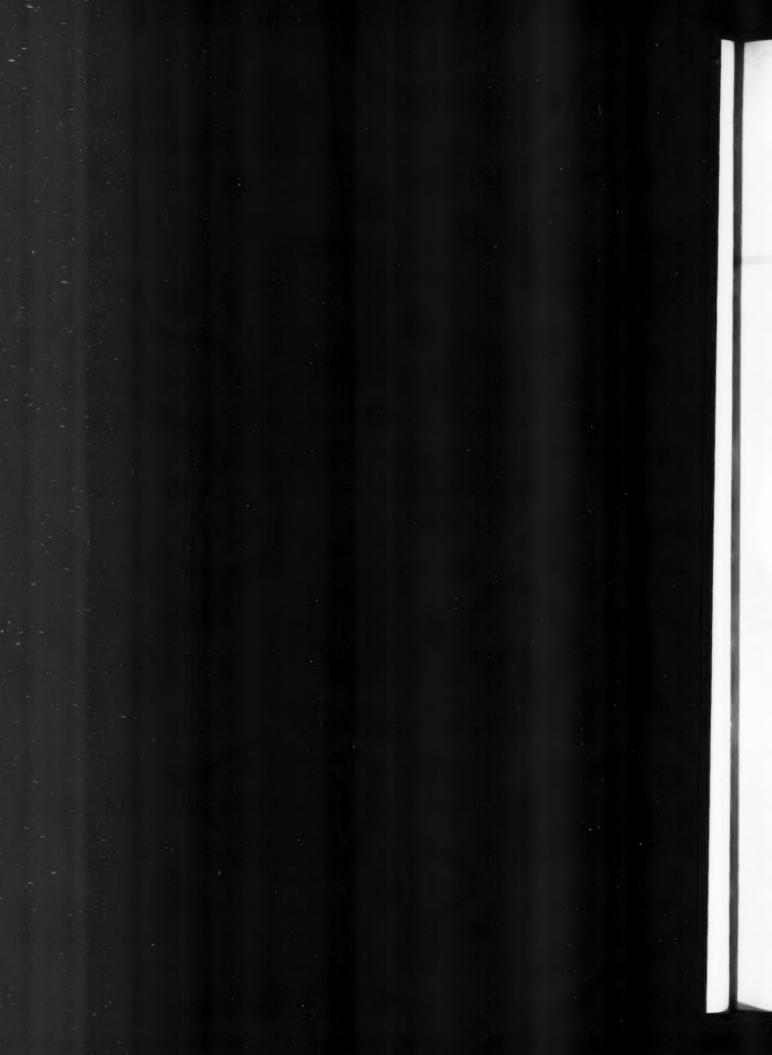
3)	Amide Ester	RCONCH2CH2OH	109
		CH2CH2OOCR	
4)	Free Diethanolamine-	HN(CH2CH2OH)2	259
5)	Fatty Acid Amine Soap	RCOONH ₂ (CH ₂ CH ₂ OH) ₂	59

Although these 2:1 type amides are complex mixtures of at least five or six different products, it seems that this balance of various products provides the amides with just the qualities which make them ideally suited for use in most cosmetic applications.

A few years ago, the chemical industry developed a new technique for condensing equimolar quantities of diethanolamine with fatty acid esters; the resultant condensates contain 90% or better of the dihydroxyethyl acyl amide. These condensates are best known today as super amides or high activity alkylolamides. The products in general use today are derived from lauric or coconut fatty acids. These high amide condensates are water dispersible materials which may be used interchangeably with the 2:1 type amides for most applications.

In the condensation of equimolar quantities of diethanolamine and fatty acid at 150-160°C, in the absence of excess diethanolamine or without the special reaction conditions used for preparing super amides, water insoluble products result. The chemical composition of the equimolar diethanolamine-fatty acid condensates has never really been completely established. The stearic derivatives of these simple 1:1 condensates are used as





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hair conditioner-rinses when formulated under slightly acid conditions. The other fatty acid derivatives of these condensates are not commonly used in cosmetic preparations.

The monoethanolamine and isopropanolamine condensates of lauric acid are produced in substantial quantities for the soap and detergent industry. These particular amides are used extensively in liquid and powdered household detergents; their use in the cosmetic field is negligible, probably because of their poorer water solubility characteristics

Alkylolamides of the 2:1 type are available under the trade designations such as ALROSOL (Geigy), Ninol (Stepan), Onyxol (Onyx), Monamine (Mona), Syn-o-tol (Drew), Ultrapol (Ultra), Hyonic FA (Nopco), etc. The 1:1 super amides are available under the designations DHL-95 (Geigy), Ninol AA Extra (Ninol), Super Amide (Onyx). The simple 1:1 diethanolamine condensates, as well as the lauric alkylolamides derived from monoethanolamine and isopropanolamine, are also available from most of these same manufacturers.

Wetting and Dispersing Properties of Alkylolamides

The water soluble, liquid alkylolamides of the 2:1 type, which include the lauric, coconut and capric acid derivatives possess good wetting properties in aqueous systems. Unlike soap, the wetting properties of these amides are relatively unaffected by hard water or acid conditions.

The water dispersible amides, which include the 2:1 condensates of oleic, myristic and stearic acids, as well as all the various fatty acid derivatives of the 1:1 super amide or 1:1 simple condensates, possess only slight wetting properties, although they do exhibit almost as good dispersing characterstics as the 2:1 type water soluble amides.

The combination wetting, dispersant and thickening properties of the amides probably explain their general acceptance in dye or pigment containing cosmetics such as hair colorants, liquid make-up etc.

Emulsifying

The water soluble lauric, coconut and capric alkylolamides of the 2:1 type are excellent oil-in-water emulsifying agents. Generally, increased emulsion stability is obtained if trace amounts of oleic acid are used in conjunction with these amides.

For silicone wax or mineral oil emulsions the oil soluble, oleic or stearic alkylolamides of any of the three types of diethanolamine condensates are the preferred emulsifying agents.

This broad range in the emulsifying characteristics of the amides permit their use in a wide variety of cosmetic emulsions.

Solubilizing

The capric and coconut 2:1 type amides are considered ideal solubilizing or coupling agents for incorporating oils or perfumes into various clear liquid cosmetic systems. The capric 2:1 amide has been found particularly effective for solubilizing high titer soaps which have a tendency to cloud soap based liquid shampoos. The super amides and simple 1:1 type condensates are generally ineffective solubilizers.

Detergency

In aqueous systems only the lauric, coconut or capric 2:1 amides are considered to be good detergents. These three type amides are probably effective as detergents

because of their excellent wetting, solubilizing and emulsifying properties. All three materials are much more effective as detergents in hard water systems than the alkaline or amine soaps of the corresponding fatty acids. Information pertaining to the effectiveness of amides as detergents has been presented in a numbr of earlier papers. Barnett & Powers developed data which indicated that alkylolamides were very effective detergents in hard or soft water for removing grease from greased wool. A fair degree of correlation was thought to exist between this test method and detergent effectiveness of shampoos in actual use in the home or beauty parlor.

Foaming and Lathering

The lauric, coconut and capric 2:1 type amides are good foaming agents themselves in aqueous systems, as well as effective foam boosters and stabilizers for alkyl aryl sulfonates and alcohol sulfates. The high activity alkylolamides, as well as the lauric monoethanolamide and isopropanolamide act as foam stabilizers and improvers in anionic systems, although they do not exhibit any foaming properties themselves in aqueous systems.

In cosmetic applications, foam deterioration is generally caused by calcium soaps, fatty acids or other oil like substances normally present on the skin or hair. Amides effectively counter the defoamant action of such materials. A number of papers have been published relative to methods for determining the effectiveness of various surfactants, including amides as foam stabilizers for anionic synthetic shampoo preparations.9.10.11 Barnett and Powers12 demonstrated that amides improved the lathering as well as the foaming properties of synthetics and also further substantiated, through consumer panel evaluation, that high foaming or lathering shampoos were preferred to non-foaming type preparations. Tests in our own laboratories verify that the lauric and coconut amides of the 2:1 or super amide type are particularly effective foam stabilizers and lathering improvers for sodium lauryl sulfate based shampoos. Lathering improvement may be determined by comparison of the sinking time of a magnesium strip through foams obtained by beating-up aqueous solutions of alcohol sulfates and alcohol sulfate-amide combinations, in the Waring Blendor, in the presence as well as absence of a defoamant. Foam stability is generally measured by shaking up similar aqueous solutions in a volumetric graduate to which various defoamants have been added. Foam heights are then compared at various time intervals. In evaluation of products for suitability as foam stabilizers or lathering improvers in shampoos, it appears to be desirable to use wool grease or sebum as the defoamant. In the evalution of bubble bath preparations a calcium soap would be the preferred material for use in checking foam stability.

Corrosion Characteristics

The amides are non-corrosive to steel. Many amides, particularly those of the 2:1 type, are incorporated in alkyl aryl sulfonate or alcohol sulfate systems because of their corrosion inhibiting properties.

Toxicity and Irritating Characteristics

Coconut, lauric or capric acid alkylolamides of the 2:1 type when used in concentrations of up to 7% have been found to be nonirritating to the eyes of albino rabbits. $^{13\cdot14}$

Cosmetic Application of Alkylolamide Shampoos

The most important application of 2:1 or 1:1 super

amides in the cosmetic field is undoubtedly their use as viscosity boosters (Graph I and II) and foam stabilizers in lauryl sulfate based shampoos. The amides in such preparations also tend to compensate for the drying action of alcohol sulfates and thus contribute to the softness and manageability of the hair. From this standpoint, the lauric or coconut derivatives appear to be most desirable for use in shampoos. The 1:1 high activity amides are better thickening agents (Graph I) than the conventional 2:1 type amides, although the former possess some disadvantages compared with the 2:1 amides in that they quite often do not provide as efficient hair conditioning and occasionally cause difficulties in formulating clear preparations due to poorer water solubility characteristics. Both types of amides improve the lathering characteristics of lauryl sulfate based shampoos considerably.

Formula 1 is typical of a professional shampoo concentrate; one pint, when diluted to a gallon with water, yields a clear water-white, viscous liquid shampoo.

The 2:1 type amides are particularly well suited for use in soap based shampoos where they not only increase viscosity and stabilize foam, but also prevent the deposition of lime soap on the hair during rinsing operations with hard water. Alkylolamides, particularly the 2:1 capric type, prevent turbidity in liquid soap shampoos where this condition is caused by the presence of small amounts of high titer soaps.

Aerosol Story (Dodge and Olcott, Inc.) suggests Formula 2 as an Aerosol type shampoo. SARKOSYL NL-30 is recommended because of its combination detergent and corrosion inhibiting properties.

Formula 1

TEA Lauryl Sulfate 50%	22.5	parts
Lauric Diethanolamide 1:1 type	22.5	99
H ₃ PO ₄ (to pH 7.0-7.5)	0.0	22
Isopropyl Alcohol	4.5	91
H.O. Perfume and Color	50.0	9.9

Formula 2

Aerosol	Sha	mpoo	
SARKOSYL NL-30	33	parts	
ALROSOL C	3	99	
Sodium Lauryl Sulfate	5	22	
Oleyl Alcohol	1	99	
TEA Lauryl Sulfate	5	99	
Water	53	93	
Concentrate	90	9:3	
Propellant	10	11	55 pounds per square inch

Bubble Baths

Lauric or coconut Kritchevsky alkylolamides are used in bubble bath preparations to stabilize foam. Usually foam deterioration in the bathtub is due to calcium soap which forms when a soap bar is introduced into the bath water. An example of typical high foaming bubble bath preparations is:

Formula 3

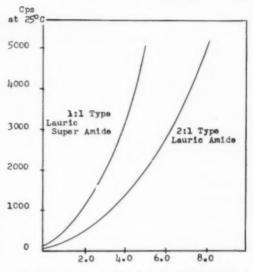
TEA Alkyl Aryl Sulfonate (60%) 2:1 Type Lauric Amide	30 20	parts
Perfume	2	99
Water	48	93

Hair Waving

Coconut or stearic alkylolamides of the 2:1 type are

GRAPH I

Effect on the Viscosity of a 20.0% Aqueous Solution of Sodium Lauryl Sulfate Upon Addition of Various Lauric Acid-Diethanolamine Condensates.



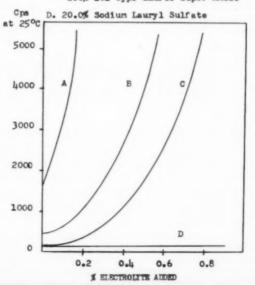
% AMIDE ADDED TO 20% SODIUM LAURYL SULFATE

GRAPH II

Effect of Addition of an Electrolyte to a Shampoo Type System Containing:

Curve

- A. 20.0% Sodium Lauryl Sulfate 4.0% 1:1 Type Lauric Super Amide
- B. 20.0% Sodium Lauryl Sulfate 4.0% 2:1 Type Lauric Amide
- C. 20.0% Sodium Lauryl Sulfate 2.0% 1:1 Type Lauric Super Amide



used as thickening and opacifying agents in sodium bromate neutralizers for cold waves. The viscosity imparted by the amide helps the neutralizer cling to the hair and thus facilitates the reforming of disulfide bonds with the mercaptan groups in the hair. The amides in such neutralizers also re-establish the luster and softness of the permanently waved hair.

Formula 4

Hair Wave Neutralizer

2:1 Type Coconut Amide	7 parts
ALROMINE RU-100	1 "
Sodium Bromate	14 "
Water	78 "

Depilatories

Coconut amides of the super amide or 2:1 type are used as wetting and thickening agents in depilatory creams.

Hair Dyes

Alkylolamides of the 2:1 type, such as ALROSOL, have been found effective in hair dye bases, color shampoo bases and dye-bleach bases. In such preparations, the amides function as viscosity builders, as well as wetting, leveling and dispersing agents for the dyes.

Hair Conditioner-Rinses

Acid aqueous dispersions of stearic acid diethanolamine condensates are quite popular in hair conditionerrinses. The amides impart softness and luster to the hair without oiliness. In addition, an antistatic protective film contributes significantly towards leaving the hair neater and more manageable. An important advantage of the stearic amides in rinses are their relatively low irritation characteristics as compared with the typical cationics more commonly used in hair rinses.

Shaving Cream

Stearic acid diethanolamide condensates, when added at 2% levels to shaving creams, increase the water tolerance of such products and greatly improve texture, appearance and spreading properties. The amide also imparts lubricity so necessary for more comfortable shaving.

Miscellaneous

Other application of amides might include their use in antiperspirants, hair dressings, cleansing, protective and emollient creams.

Conclusion

Fatty acid condensates of monoethanolamine, isopropanolamine and diethanolamine are the three general types of alkylolamides which are of commercial importance. Alkylolamides, particularly those derived from diethanolamine, have become increasingly important to the cosmetician during the past 10-15 years.

Alkylolamides are generally used in conjunction with other surfactants in order to improve or modify the surface active properties of the base detergent. Due to the effectiveness of these amides as viscosity builders, detergency improvers, foam stabilizers, emulsifiers, dispersants or wetting agents, they are used for almost all major cosmetic applications. Cosmetic systems which frequently contain amides might include: shampoos,

bubble baths, depilatories, shaving creams, hair dyes, dressings, neutralizers and rinses.

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The following trade names were used in the paper. Most of these are trademarks registered with the U.S. Patent Office:
Syn-o-tal

Function of a Sunscreen

Ninol AA Extre

Ultrapel

Mona Industries, Inc. Paterson, NJ

Nopco Chemical Co. Harrison, NJ

Stephen Chemical Chicago, III.

Ultra Chemical Works Paterson, NJ

Onyx Oil & Chemical Co Jersey City, NJ

The function of a cosmetic sunscreen in a suntan preparation is to absorb as completely as possible the sun's erythematogenic ultra violet radiation while it transmits a maximum of all the other wave lengths of the sun's radiant energy, Dr. Saul I. Kreps, technical director of Van Dyk & Co. told the members of the New York Chapter of the Society of Cosmetic Chemists.

Such a preparation will effectively prevent painful sunburn and at the same time permit adequate tanning. Few chemicals come close to meeting this ideal situation but it is possible to design useful compounds from a knowledge of the radiant energy required by certain configurations in passing from one energy level to another and the efficiency of such transitions.

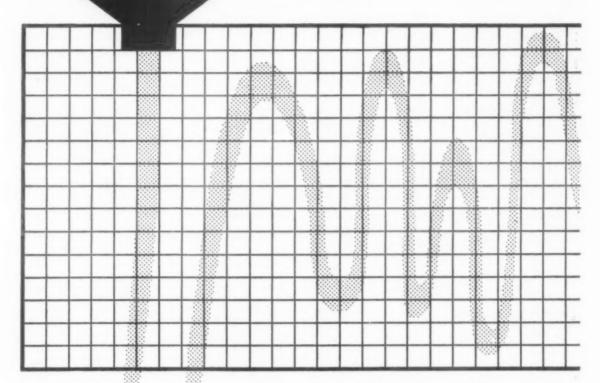
The erythematogenic or "burning" wave lengths of solar radiations extend from about 290 to 315 millimicrons. By the use of Planck's Equation it has been shown that an effective sunscreen must contain a molecular configuration having a transition energy requirement between 91.4 and 99.4 kilogram calories per gram-mole in order for the chemical to exhibit maximum absorption in the "sunburning" range.

The quinoid structure is the most useful as the basis for developing a practical sunscreen. Benzene has a maximum absorption at 180 millimicrons and at 200 millimicrons—much too far in the ultraviolet—but substitution of an amino group for a hydrogen yields aniline with maximum absorption at 230 millimicrons. Introduction of a carboxylic group rara to the amino shifts the absorption maximum further to 290 millimicrons—just within the erythematogenic band. However p-aminobenzoic acid is not a useful suncreen because its ionization impedes the formation of the quinoidal structure. When the acid is esterfied, ionization is prevented and the ester becomes a practical cosmetic sunscreen.

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In lipsticks, acetoglycerides enhance plasticity and reduce bleeding under wide variations of temperature.

Send for Technical Information Bulletin 227. It describes the various grades of ABRAC Acetoglycerides in full detail, and gives suggested formulae for their inclusion in creams and lipsticks.

Imports of Vanilla and Tonka Beans During the Year 1957 and First Quarter of 1958

Monthly statistical data on importation of vanilla beans and tonka beans during the year of 1957 and the first three months of 1958, as compiled by the U. S. Department of Commerce is as follows. The compilation sets forth the pounds, dollar value, and country of origin received from during said respective months. The subtitle "Other Cty." includes countries from which imports are less than \$10,000.

(Statistical	Data on	Imports o	f Vanilla	Beans-1957)	ı
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Country	Lbs.	Dollar Valu
French Pacific Islands	12,559	67,391.
Madagascar	28,665	149,605.
Other Cty.	3,529	16,389.
(January) Total	44,753	233,385.
Mexico	14,080	67,733.
French Pacific Islands	9,389	47,833.
Madagascar	108,097	567,123.
(February) Total	131,566	682,689.
Mexico	17,352	73,214.
French Pacific Islands	8,130	47,660.
Madagascar	148,458	842,978.
Other Cty.	146	947.
(March) Total	174,086	964,799.
Mexico	25,508	159,406.
French Pacific Islands	10,977	66,737.
Madagascar	142,961	915,579.
Other Cty.	2,138	6,672.
(April) Total	181,584	1,148,394.
Mexico	41,254	252,077.
French Pacific Islands	4,098	24,464.
Madagascar	102,518	610,576.
Other Cty.	331	545.
(May) Total	148,201	887,662.
Mexico	32,440	221,058.
Madagascar	30,987	183,545.
Other Cty.	3,533	14,712.
(June) Total	66,960	419,315.
Mexico	3,282	14,751.
French Pacific Islands	3,410	21,100.
Madagascar	118,247	770,387.
Other Cty.	1,223	7,119.
(July) Total	126,162	813,357.
Mexico	16,977	118,839.
French Pacific Islands	2,205	13,400.
Madagascar	44,310	295,357.
Other Cty.	794	4,851.
(August) Total	64,286	432,447.
Mexico	20,107	129,168.
France	3,611	10,745.
French Pacific Islands	12,612	74,657.
Madagascar	75,800	644,815.

Other Cty.	420	2,789.
(September) Total	112,550	862,174.
Mexico	30,086	223,952.
French Pacific Islands	9,172	52,781.
Madagascar	30,254	198,057.
Other Cty.	1,204	3,249.
(October) Total	70,716	478,039.
Mexico	7,982	53,498.
Madagascar	73,688	487,805.
(November) Total	81,670	541,303.
Mexico	8,005	59,944.
France	4,038	11,383.
French Pacific Islands	5,465	30,510.
Seychel	2,075	12,394.
Madagascar	25,958	170,026.
Other Cty.	2,205	3,636.
(December) Total	47,746	287,893.

1958 Vanilla Bean Imports

1390 1 441111	a Dean Impor	15
Mexico	4,908	36,807.
French Pacific Islands	12,104	66,679.
Madagascar	95,320	628,231.
Other Cty.	774	5,717.
(January) Total	113,106	737,434.
Mexico	16,524	82,726.
French Pacific Islands	3,535	20,879.
Madagascar	65,833	431,578.
Other Cty.	4,617	12,861.
(February) Total	90,509	548,044.
Mexico	15,102	111,112.
British East Africa	1,456	10,620.
Madagascar	204,900	1,416,225.
Other Cty.	3,354	16,442.
(March) Total	224.812	1.554.459

1957 Tonka Bean Imports

Other Cty.	6,764	4,420.
(January) Total	6,764	4,420.
No Imports for the Mon		F 100
Other Cty.	6,457	5,106.
(March) Total	6,457	5,106.
Other Cty.	264	317.
(April) Total	264	317.
Other Cty.	6,022	4,731.
(May) Total	6,022	4,731.
Other Cty.	8,472	7,081.
(June) Total	8,472	7,081.

ontinued on page 88

NONIONIC SURFACTANTS

Based on

ALKYLPHENOLS and ALKYLMERCAPTANS







Raymond L. Mayhew is program manager in charge of Chemical Specialties Research at the Central Research Laboratory of General Aniline and Film Corp., Easton, Pa., where he has been employed since 1944. He received his Ph.D. degree from Purdue University in 1944. He has been engaged in research both synthetic and applied in the fields of surfactants, detergents, emulsification, polymers and related materials. He has published numerous articles and is the author of a number of patents in these fields. He is a member of the ACS, AATCC and N.A.C.E.

It is estimated that upwards of 200,000,000 pounds of nonionic surfactants will be sold in 1958. Two important members of this rapidly growng class of surfactants which perform at high-level in the various areas of surfactant activity—wetting, emulsification, detergency, dispersing, penetration, and foam—are those prepared by reacting ethylene oxide with (1) alkylphenols and (2) alkylmercaptans. These products have other major advantages for specialty compounders such as chemical stability, compatibility in formulations, ease of handling, and uniformity. The availability of individual products tailored to emphasize favorable combinations of both functional and non-functional properties for major uses has also contributed to their market success.

Properties

Polyoxyethylated alkylphenols and polyoxyethylated alkylmercaptans have certain properties in common. Their nonionic nature insures compatibility with either anionics or cationics and they may be compounded with soap. Both are essentially unaffected by water hardness and are efficient over broad temperature and pH ranges. They are available in concentrated form, virtually free from unreacted base materials.

However, differences in chemical structure naturally influence behavior. The alkylphenol-ethylene oxide adducts contain the ether linkage which insures chemical stability in either acid or alkaline systems and these

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surfactants are used regularly in operations above 400° F. On the other hand, the thioether linkage of alkylmercaptan-based nonionics is unstable in strongly acidic media, though these surfactants are perfectly stable under neutral or alkaline conditions and may be used above pH 3 in dilute, non-oxidizing acids. Moreover, the thioether type nonionics exhibit outstanding stability in strong, hot alkali.

In the presence of oxidizing agents, the alkylphenol-based products are not affected but the thioether linkage of the alkylmercaptans is sensitive to peroxide and to hypochlorite bleach. Advantage, however, can be taken of the characteristic ease with which the sulfur to carbon bond may be broken to oxidizing agents or chlorine in processes where it may be desirable to destroy the surface active agent at a certain point in an operation. For example, rapid inactivation of the surfactant can be useful where it is desirable to terminate foaming or emulsification at a given step in the procedure. Likewise, inexpensive chlorine treatment of process effluents could eliminate disposal problems of residual surfactant. The oxidizable sulfur also offers a practical advantage in quantitative analysis.

Several reports have appeared in the literature which detail the surface active characteristics of these two types of nonionics (1-6).

Chemistry

Ethoxylation of alkylphenols and of alkylmercaptans proceeds as shown below; both I and IV react more

^{*}General Aniline & Film Corp., Central Research Laboratories, Easton, Pa.
**Antara Chemicals Division of General Aniline & Film Corp., New York, N.Y.

readily with ethylene oxide than II and V.

alkylphenol

$$\begin{array}{c} CH_2-CH_2 \\ R-SH \xrightarrow{+} O \\ \hline IV \\ V \\ \end{array} \longrightarrow R-S-CH_2CH_2OH \xrightarrow{+} O \\ \hline V \\ VI \\ alkylmercaptan \\ \end{array}$$

In the case of alkylphenols, the alkylylate may vary from C_5 to C_{15} and may be mono-, di-, or trisubstituted on the phenol. However, there are relatively few alkyl phenols used in commercial surfactant production. The most common are octyl-, nonyl-, dodecyl-, dinonyl-, and pentadecylphenol.

$$C_{9}H_{17}$$
 (OCH₂CH₂)_nOH $C_{9}H_{19}$ (OCH₂CH₂)_nOH OCTYLPHENOL NONYLPHENOL

$$(C_9H_{19})_2 \qquad (OCH_2CH_2)_0OH \qquad C_{12}H_{25} \qquad (OCH_2CH_2)_0OH$$

DINONYLPHENOL DODECYLPHENOL

To prepare the alkylphenol, an olefin is reacted with phenol in the presence of a suitable catalyst and the endproduct is distilled to insure uniformity. It is significant that the alkylphenols most widely employed for the preparation of nonionic surfactants are the only hydrophobic base materials that produce a 100% active, colorless, odorless, homogenous liquid nonionic having the hydrophobic-hydrophilic balance most desirable for general industrial surfactant purposes. The thioether nonionics tend to have an odor problem but this may be overcome by treatment with superheated steam (7).

The olefins commonly used for surfactant production are amylene, diisobutylene, tripropylene, tetrapropylene, and 2-ethylhexane. Ethylene oxide is added to the alkylphenol in the presence of an alkaline catalyst under anhydrous conditions. The addition of the first mol of ethylene oxide is essentially quantitative before further polymerization takes place because the alkylphenol hydrogen is more reactive than the alkylphenoxyethyl hydrogen (4). Under normal production conditions this assures virtual freedom from unreacted base materials in the nonionic surfactant. The chaining out of the ethylene oxide is a random reaction, but by proper control, the average chain length can meet rigid specifications. In fact, reproducibility in the end product is remarkable in large scale commercial production and there is very little difference in color, odor, solubility, and performance among different lots produced at any predetermined mol ratio.

Although R may also vary over a wide range in the ethoxylated alkylmercaptan series, a $\rm C_{12}$ -branched chain hydrocarbon based on triisobutylene or tetrapropylene is the most practical commercially.

Since these surfactants may be modified by varying the molecular weight, alkyl group, or amount of ethylene oxide in a given product, producers are able to offer homologous series prepared from several base materials, providing a broad spectrum of physical and chemical properties and performance ranges. This allows the formulator to select the product with the desired balance for optimum performance in a specific case. In certain instances, mixtures of nonionics may be formulated to meet special requirements.

Effect of Mol Ratio

Surfactants prepared from ethylene oxide are not single compounds but mixtures of compounds with different mol ratios of ethylene oxide. The composition of a nonylphenol nonionic follows the Poisson distribution curve (2). Thus the mol ratio refers to an average value. The mol ratio distribution is such that, for a 10-mol product, about 80 percent by weight is within the range of 8 to 16 mols of ethylene oxide (4). In certain applications, i.e. emulsification detergency, and for specific solubility, a wider spread of mol ratio distribution is desirable.

Changing the amount of ethylene oxide on nonylphenol from $1\frac{1}{2}$ (23 percent) to 30 mols (86 percent) changes physical and chemical properties (Table I).

Table I

Alkyl Phenol Constant-Varying Ethylene
Oxide Nonylphenol Base

		% EtO	Mol Ratio	Physical Form		Pt. H _t O F.	R-M Foam .05% H ₂ O 77° F.
Igepal	CO-210	23	11/2	liquid	ins		-
	CO-430	44	4	liquid	ins		-
	CO-510	54	6	liquid	ca	32	28
	CO-630	65	10	liquid		130	61
	CO-710	68	11	eld. liq.		160	79
	CO-730	75	15	soft pst.		200	110
	CO-850	80	20	paste	ca	200	118
	CO-880	86	30	wax	ca	240	106

Usually the shorter chain lengths are effective foam control agents and cosolvents. Surfactants containing 44 percent to 65 percent ethylene oxide are good emulsifiers with the phase shifting from water in oil to oil in water as the chain length increases. For all-around performance, alkylphenol-based nonionics containing 65 percent to 75 percent ethylene oxide are in wide general use. With more than 75% ethylene oxide, these nonionics function as stabilizers for latices, as dispersants for solids in aqueous systems, and as detergents or emulsifiers in strong electrolyte systems. As the percent ethylene oxide increases, the molecular weight increases, the cloud point goes up, and the initial foam in the Ross-Miles test goes through a peak at about 80 percent ethylene oxide. Detergency, as measured from the reflectance of cotton after washing, remains fairly level over the range of water soluble products (8).

Table II shows several physical and chemical variables when four different alkylphenols are treated with enough ethylene oxide to give equivalent water solubility to all resulting products.

Table II

Ethylene Oxide Constant-Varying Alkylphenol

	12 in yee ne	Ozenn	Consu	int-vary	iny za	ingiphenoi	
	%	Mol	M.W.	Cld. Pt.	Solid	Form	R.M. Foam .05% Ml.
Base	EtO	Ratio		°F.	${}^{\circ}F$.	Physical	77° F.
MOP	67	9.5	625	130	15	Liquid	66
MNP	65	10.0	660	128	26	Liquid	61
DDP	65	11.0	750	130	56	Cld. Liq.	38
DNP	64	15.0	1000	125	60	Soft Pst.	30

MOP-Mono Octylphenol DDP-Dodecylphenol MNP-Mono Nonylphenol DNP-Di Nonylphenol

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(A creamy, pure white paste)

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ANTARA







Moving up in the series from actyl to dininyl, it requires almost 50 percent more ethylene oxide (9.5 to 15 mols) to give similar cloud points. There is an increase in molecular weight of 60 percent. Physical form varies from a liquid to a paste as the solidification point moves upward from 15° to 60°C. Ross Miles foam tests show a definite decline in foam with increased molecular weight.

There are certain significant advantages to the higher molecular alkylphenols. When the water soluble types are tested for detergency there are small but distinct improvements in whiteness reflectance of cotton as the molecular weight of the alkylphenol increases. When the oil-soluble types are tested for emulsification there is a definite improvement in the stability of the emulsion. Oddly enough, increasing the alkylation does not necessarily improve the solubility of the nonionic in solvents.

The effect of increasing the length of the polyglycol chain in the thioether nonionics is much the same as for the phenol-ethoxylated products discussed above. As the mol ratio of ethylene oxide to alkylmercaptan becomes higher, the hydrophilic properties progressivly increase (as evidenced by greater solubility), the cloud point is raised and there is greater tolerance for electrolytes in formulations. The lower mol ratios exhibit predominately hydrophobic properties, i.e. greater oil solubility and lower cloud point.

Ethoxylated alkyl mercaptans are commercially available with mol ratios of 1 to 10. (9).

Product	Mol Ratio
Nonic 218	9-10
Nonic 234	8-9
Nonic 259	1
Nonic 260	5-6

The first compound listed above is based on tertiary dodecyl mercaptan and exhibits a wide range of usefulness. However, in most cases it is not possible to predict comparative performance, and the thioether-type nonionic for a specific job is best established by suitable trial. For example, kerosene is emulsified by compounds with a mol ratio of 6; certain silicones, 10; and some waxes, 25. Lower mol ratios give less foam and enhance wetting action with some loss in detersive efficiency. The product containing only one ethylene oxide unit is actually an aliphatic alcohol, but is more readily emulsified. At mol ratios above 11, thioether nonionics are not homogenous liquids at room temperature and above 15, are soft, semisolids of soapy consistency. The tendency is toward waxiness as the ratio goes higher.

Toxicity

In tests (10) on three classes of surfactants—anionic, cationic, and nonionic—the nonionic products as a group were found least toxic. However, in accordance with the usual trade custom, it is advisable to test all new cosmetic formulations containing surfactants for possible irritation before marketing. In the case of the alkylphenols or alkylmercaptans, thorough ethoxylation minimizes any physiological response which may be associated with the free base material. All tests indicate these nonionics are safe to use in the concentrations recommended by the manufacturers. These products are not intended for internal consumption.

Acute Oral Toxicity (LD50)

	rats	guinea pigs	
Igepal CA-630	4.25 cc/kg	1.65 cc/kg	
Igepal CO-430	5.0 cc/kg	6:0 cc/kg	
Igepal CO-630	3.0 g/kg	2.0 g/kg	
Nonic 218	1.84	g/kg	

Members of the alkylphenol nonionic family have been subjected to extensive skin and eye irritation tests. Results indicate these materials are neither primary irritants nor sensitizers. While care should be taken to avoid direct contact with the eyes, Igepal CO-630 can be used in shampoos in concentrations up to 5%. In the case of Nonic 218, it seems safe to conclude that up to 1% aqueous solution (the highest concentration normally employed) will be safe for external application and will not cause primary skin irritation or sensitization (11).

The nonionics discussed here are generally considered to be less defatting and less irritating to the skin than many other surfactants.

Cosmetic Applications

As would be expected, the versatility of these nonionic surfactants find many uses in the cosmetic industry. In liquid soap shampoos, for example, such materials as Igepal CO-630 and Nonic 218 improve rinsability of the formulation and its effectiveness in hard water. Excellent lime soap dispersion prevents deposition of a dulling film, i.e. insoluble soaps, on the hair. Since these products possess a wide range of emulsifying properties, they have been widely used also in formulating creams and lotions for a variety of uses.

These products are valuable dispersing agents and, at concentrations of 0.1%, are effective in dispersing tale, diatomaceous earth and similar products. They are also effective solubilizing agents and in certain instances act as detoxifying agents.

Typical Formulations

Hair Groom

- 15.0 parts heavy mineral oil
- 7.5 parts Igepal® CO-530
- 7.5 parts Igepal® CO-430
- 1.5 parts Alipal® Co-436
- 68.5 parts water
- q.s. perfume

Add the surfactants to the mineral oil and mix well. Then add the water slowly with stirring to give a rich white stable emulsion which is useful as a hair groom.

Hand Cream

- 10.0 parts stearic acid
- 9.0 parts Igepal® CO-850
- 5.0 parts propylene glycol
- 76.0 parts water
- q.s. preservative and perfume

Brushless Shave Cream

- A. 17.5 parts stearic acid (triple pressed)
 - 2.5 parts Emulphor® VT 679
 - 1.0 part Igepal® CO-710
 - 5.0 parts White Petrolatum
- B. 5.0 parts Propylene Glycol 67.0 parts water
- C. 2.0 parts 28% ammonia water

Melt (A) and heat to 80°C, heat (B) to 82°C. Charge (C) to (B) quickly add to (A) with moderate agitation. Stir until the batch cools to 55°C. Perfume and stir slowly until the temperature is 45°C. Stir for 2-3 days at room temperature. Remix and pack in suitable containers.

Aerosol Shave Cream

- A. 1.0 part stearic acid
 - 1.0 part stearic acid
 - 2.4 parts cetyl alcohol1.5 parts Hydrous Lanolin
 - 4.8 parts Heavy Mineral Oil



A water-white, liquid saturated fatty alcohol,
Non-irritant, almost odourless,
Easy penetration through the epidermis,
Excellent vehicle for lipoid soluble active ingredients,
Dermatologically approved.
For the preparation of liniments, sun-tan oils,
cosmetic creams, emulsions, lipsticks, hair lotions,
shampoos, toilet soaps, shaving creams, and aftershaves.



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- B. 16.2 parts Avitex C (DuPont) 27.0 parts Avitex SF (DuPont) 3.0 parts Igepal® CO-630
- C. 43.9 parts water

® Trademark of General Aniline & Film Corp.

Heat (A) to 71°C, mix (B) with half of (C) and heat to 71°C. Add (A) to (B) with stirring. Mix (B) with half of (C) and heat to 71°C. Add (A) to (B) with stirring. The remainder of (C) is added and the batch is thoroughly mixed. The mixture is allowed to cool to 50°C, perfumed, and then cooled to room temperautre. It is reworked at room temperature and packaged with suitable propellants.

Non-foaming Shampoo (12)

20 parts Nonic 218 (Pennsalt)

5 parts Lanolin

1 part Arlacel C* (Atlas Powder)

2 parts Sodium Carboxymethylcellulose (high viscosity)

72 parts water

q.s. Preservative, perfume etc.

Mix the oils together and then add to the CMC-water gel with vigorous stirring. The viscosity may be varied with the type and quantity of CMC used.

Commercial Suppliers

Ethoxylated alkylphenols were first synthesized in Germany (5) about 25 years ago. Small quantities were imported until production was started in this country in 1937. Now broad market acceptance has led to high tonnages by several national and local suppliers. The thioether type nonionics were likewise developed abroad in the mid-thirties (13). However, it was not until after 1940 that economical processes for alklymercaptans were developed and the oxyethylated products brought into commercial prominence. These processes permit the direct addition of hydrogen sulfide to an olefin in the presence of a catalyst (14, 15).

While it is impossible to list every trade name or every supplier of alkylphenol-ethylene oxide adducts, the following list may be considered representative. The alkylmercaptan-based products are specialty items available from only two manufacturers at the present time.

Ethoxylated alkylphenol nonionic surfactants

Arctic Syntex (Colgate-Palmolive Co.) Atcopal (Metro-Atlantic) Dispersant (Oronite Chemical Co.) Energetic (Armour and Company) Hyonic (Nopco Chemical Co.) Igepal (Antara Chemicals Division of General Aniline & Film Corp.) Kyro (Procter and Gamble Co.) Lipal (E. F. Drew and Company) Makon (Stepan Chemical Co.) Neutronyx (Onyx Oil and Chemical Co.) Ninol (Ninol Laboratories Inc.) Nonic (Pennsalt Chemicals Corp.) Polytergent (Olin Mathieson Chemical Corp.) Renex (Atlas Powder Co.) Solar (Swift and Company) Sterox (Monsanto Chemical Co.) Surfonic (Jefferson Chemical Co., Inc.) Synthetics (Hercules Powder Co.) Tergitol (Union Carbide Chemicals) Triton (Rohm and Haas Co.)

In summary, the alkylphenol-based nonionics are among the most widely utilized surfactant materials.

They have excellent color and odor stability and are available from large scale production by national and local suppliers. Their chemical structure provides unusual stability, even under extreme conditions of pH or temperature. Their versatility has pushed these nonionics to the top of the ethlene oxide-based surfactant market.

The thioether-type nonionics represent a unique class with especially good wetting, penetrating, and lime soap dispersing properties. An inherent facet of their chemical structure is susceptibility to inactivation through oxidation. However, in our competitive economy, the many advantageous properties possessed by this group of surfactants will find increasing use in the development of new products.

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Imports of Vanilla and Tonka Beans During the Year 1957 and First Quarter of 1958

Continued from page 82

Country	Lbs.	Dollar Value
Other Cty.	3,307	3,638.
(July) Total	3,307	3,638.
Venezuela	16,170	18,592.
Other Cty.	6,849	5,709.
(August) Total	23,019	24,301.
Other Cty.	8,238	6,613.
(September) Total	8,238	6,613.
Venezuela	38,135	41,950.
Other Cty.	8,817	8,192.
(October)	46,952	50,142.
Trinidad	21,478	22,816.
Venezuela	11,420	12,167.
Other Cty.	9,496	7,806.
(November) Total	42,404	42,789.
Other Cty.	2,204	1,543.
(December) Total	2,204	1,543.
1958 Tonk	ca Bean Impor	ts

Other Cty.	5,995	4,710.
(January) Total	5,995	4,710.
Other Cty.	5,511	4,739.
(February) Total	5.511	4.739

No Imports for the Month of March.

C2

^{*}Folyalcohol anhydride elels asid setes.

2 TEST REPORTS OF GREAT SIGNIFICANCE

DR. LOUIS C. BARAIL

Consulting Biochemist and Foxicologist 10 EAST 43RD STREET NEW YORK 17, N. Y.

No. T-17

The Miranol Chemical Company, Inc. 275 Colt St., Irvington, N. J.

EYE IRRITATION TEST

We have tested your sample of 20 per cent Miranol C2M for eye irritation according to the method of Draise. Woodard and Calvery.

O.1 cc of the sample was instilled in the conjunctival sac of rabbits.

One eye was used for the test, while the other eye was used as a control. The eyes of the animals were observed after 1, 24 and 48 hours.

The following results were obtained on the cornea, iris and Instilled eyes ctiva:

Corned	1	hour 0	24 hours 0	0 0
A. opacity B. area of cornea involve	red	0	0	0
Conjunctiva A. redness B. chemosis	Totals	0 0 0	0 0 0	0 0
	Control ey	es 0	0	0

The above results showing the total readings of 0, 0 and 0 after 24 and 48 hours indicate that the submitted sample of Miranol C2M is not irritating to the eyes of rabbits.

Respectfully submitted

Dr. Louise Barail Dr. Louis C. Barail

DR. LOUIS C. BARAIL

Consulting Biochemist and Toxicologist

IO EAST 43RD STREET NEW YORK 17. N. Y.

The Miranol Chemical Company, Inc. 275 Coit St., Irvington, N. J.

SKIN IRRITATION TEST REPORT

We have examined a sample of 20 per cent Miranol C2M to determine whether it contains primary skin irritants. The method used was the animal introdermal single injection method.

0.5 cc of a 5 per cent solution of the sample was injected with asseptic precautions introdermally into rabbits. As a control, 0.5 cc of a 5 per cent solution of olive oil castile shampoo was also injected under the same conditions into the animals.

Twenty-four hours after the injection, the animals were observed for the presence of skin irritation in comparison with that of olive oil castile shampoo.

Samples

Reaction on skin

20 per cent Miranol C2M Olive oil castile shampoo

Legend No irritation

No Interior
 + Slight reaction
 + Definite reaction
 + Very definite reaction
 + Very definite and spreading reaction

The above results indicate that the sample of 20 per cent Miranol C2M is not irritating when injected introdermally into rabbit skin.

Respectfully submitted

Dr. LouiscBarail

Dr. Louis C. Barail

A NON-IRRITATING AMPHOTERIC SURFACTANT

MIRANOL C2M CONC.*

MIRANOL C2M CONC. is a new amphoteric surface active agent which is completely non-irritating as proved by laboratory tests. Chemically it is a dicarboxylic analogue of MIRANOL CM CONC., the coconut derivative of the MIRANOL M SERIES. The product has a pH of 7.8 measured directly and 8.1 in 20% solution in local tap water.

As the intradermal injection test report shows (the severest test of is kind) MIRANOL C2M CONC. caused no reaction (-) whereas the accepted standard for mildness (Olive Oil castile shampoo) caused a "definite reaction" (+ +). Water causes a slight reaction, thereby proving to be more irritating than MIRANOL C2M CONC. Practically all surfaces active agents

Where the complete absence of irritation is desirable, MIRANOL C2M CONC. should be used. It is recommended for the formulation of shampoos, hand soaps, color rinses, hygienic products, medicated soaps, skin cleaners, liquid bubble bath and other non-irritating specialties designed specifically for use in cosmetic and pharmaceutical preparations. As a shampoo, MIRANOL C2M CONC. is a profuse and instant flash foamer, even on first application. Due to its substantivity, the hair is left in excellent and manageable condition. Crystal clear products with exceptional temperature stability can easily be formulated.

MIRANOL C2M CONC., when combined with normally irritating surfactants, will materially reduce or even completely eliminate all irritating properties.

Send for sample today

*U. S. Patent No. 2,773,068

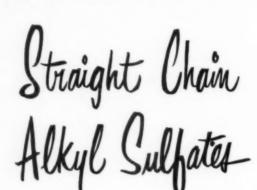
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THE DEVELOPMENT AND USE OF ...



ERNST GOETTE and GUENTER MEINHARD*



Dr. Ernst Goette

Dr. Ernst Gaette became known as colloid chemist through his many publications in the field of surface active agents since 1931, and has made a decisive contribution to the developments of test methods. After World War II Mr. Goette did temporary work at the Department of Applied Science in Tanning Research, Institute of Scientific Research of the University of Cincinnati, Ohio.

he introduction of salts of primary alkyl sulfates—at that time known as fatty alcohol sulfonates-was the first really important development beyond soaps, sulfonized oils, and alkyl naphthalene sulfonates. Their widest application in technology came therefore very fast. The groups of synthetic detergents, such as alkyl sulfonates, secondary alkyl sulfates, alkyl benzol sulfonates, as well as noniogen ethylene adducts with fatty acids, fatty alcohols, and alkylphenols, which were developed in later years, could not diminish the importance of primary alkyl sulfates. Their use is constantly increasing. Through the joint research by the Deutsche Hydrierwerke GmbH, under Schrauth's (1) direction and the Böhme Fettchemie GmbH. (2), alkyl sulfates were developed since 1928 first as auxiliary agents in the textile and leather industries, and later as raw materials for detergents. They soon became generally known in Germany as fine detergents for the household under the trade mark of Fewa®.

General characteristics of alkyl sulfates

Alkyl sulfates are, next to soaps, certainly the most intensely investigated group of the anionic deterging, wetting, dispersing, and cleansing agents. The comprehensive treatise by Goette (3) provided a survey of the scientific research with this group of surface agents, made public until the beginning of 1954. In the meantime the scientific material has been further accumulating rather fast. Since alkyl sulfates can be easily prepared in pure form, and since they deliver neutral solutions, which

are not subject to hydrolysis, they are easier objects for studies than soaps. The extensive physical and colloidchemical tests with them have greatly added to the clarification of solutions and the operation of all the other colloid electrolytes. The characteristic properties of surface agents with alkyls of different length, are conditioned by the sudden and great increase of solubility at certain temperatures, which can be easily determined through the Krafft-points, as well as by concentrations, in which formation of larger aggregates—the micellesbegins. We have combined in table 1 the Krafft-points of primary alkyl sulfates according to M. Raison (4), and the critical concentrations for formation of micelles of the purest alkyl sulfates, as was recently ascertained by Kling and Lange (5) from surface tensions of acqueous solutions against n-heptane at 50°C.

Table 1: Krafft-points and critical concentrations for formation of micelles (CMC) of primary alkyl sulfates

C-atoms	Krafft-points temp. 0° C.	CMC g/1
8		22.8
10	8	8.3
12	21	2.3
14	35.8	0.70
16	43.0	0.22
18	57.5	0.070

For further characterization of the dependence of the qualities of primary alkyl sulfates on the length of their alkyls, we refer to wetting immersion tests with cotton

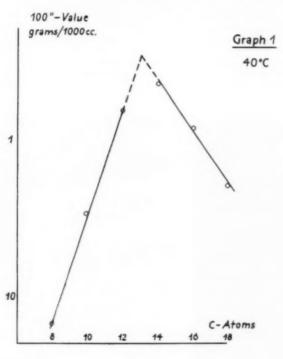
^{*}Doutscho Hydrierwerke GmbH. Dusseldorf, German

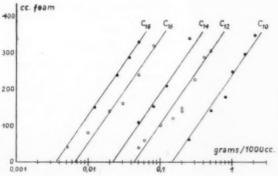
wool and to measurements of the foaming capacity, according to German standard methods (6,7). Graph 1 gives a summary of concentrations (g/1), which are just sufficient enough to achieve a thorough wetting of cotton wool, as a type of hard-to-wet fiber, in 100 seconds at 40° C. An alykl sulfate with 13 C-atoms in the alkyl would have maximum effect, and of the adjoining evennumbered products, C_{14} is somewhat superior to C_{12} (8).

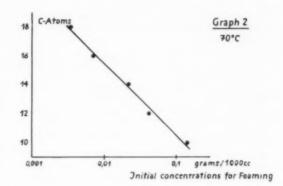
We have compiled in graph 2 measurements of the foaming capacity of homologous alkyl sulfates in distilled water at 70° C. The amounts of foam produced by uniform beating in each 200 ml. of the test solution depend lineally on logarithms of alkyl sulfate concentrations. Theresult is a multitude of paralles for the separate members of the series, as long as limits of solubility are not exceeded. The points of intersection of the straight line with the abscissa gives the concentrations, at which under chosen constant conditions the foaming sets in. The logarithms of these values depend likewise lineally on the number of C-atoms in the alkyls.

From the technological viewpoint four qualities above all make the position of primary alkyl sulfate secure:

 The possibility to choose the best suited homologues for all operational requirements, as they appear in practice, and to produce solid as well as fluid products.







- They have a positive ability to combine with other anionic and non-ionogenic surface active agents.
- 3. They are well tolerated by the skin.
- Their quick and complete biological decomposition in water processing installations.

Raw materials and manufacture

Of special interest in primary alkyl sulfates is their great inflection capability, because the widest variety of fats and oils can be used as initial bases, with the same diversity as is the case with soaps. A summary by Lindner (9) shows the structure (in %%) of some of the most frequently used raw materials.

C-atoms in the alkyl	Tallow	Hydr. tallow	Hydr. sperm oil	Sperm alcohols	Coconut
8	-	-	_	-1	
10		-)		- (15
12		}	21	_ ′	40
14	4	3		_	30
16	30	29	40x	60x)	
18 sat.	16	68)	27	12	15
18 non-sat.	50	-1	21	24	
20 and higher	-		12	4	_

x) partially non-saturated

Fatty acids provide us, after reduction with high pressure, with predominantly saturated fatty alcohol mixtures with 8-20 C-atoms, which as far as necessary are split up through distillation, and which can be separately esterified with sulfuric acid. For neutralization purposes one can choose caustic soda lye, caustic potash lye, ammonia, or organic bases such as triethanolamine as well. A further possibility would be alkyl sulfates with an oleic base; oleic sodium sulfate is one of the most effective fine detergents, because as a dodecylsodium-sulfate it has a still better solubility. Typical fine detergents and raw materials for shampoos with outstanding solubility, definite wetting capacity in cold water, and quick foaming action, can be derived from alcohol fractions C12 and C14, while sections from preferably C_{16} and C_{18} alcohols are suited for washing processes at higher temperatures. The octadecylalcohol produces a valuable partially sulfurized and with NaOH neutralized avivage agent for synthetic silks.

The addition of up to 3 mol. of ethylene oxide to fatty alcohols before their sulfurization, results in polyether sulfates with specific and valuable characteristics, such as greater hydrophilic quality, better foaming effect, and

above all higher cleansing power.

The manifold possibilities provided by the use of primary alkyl sulfates are not reached by any of the other raw materials for detergents of the anionic type.

Primary alkyl sulfates are offered on the world market

under many trade names. The following table contains a few examples and no attempt has been made to give a complete listing.

Manufacturer	Trademark®	Country
Deutsche Hydrierwerke		
GmbH., Dusseldorf	Texapon	Germany
Du Pont Co., Inc	Duponol	USA
Marchon Products Ltd.	Empicol	England
Procter & Gamble Co.	Orvus	USA
Stepan Chemical Co.	Stepanol	USA
Tensia, Société des Produits		
Tensio-Actifs & Dérivés	Tensapol	Belgium
Sinnova (France)		USA &
Am. Alcolac (USA)	Sipon	France

The application and use of primary alkyl sulfates in the pharmaceutical and cosmetic fields, based on the experience of the Deutsche Hydrierwerke GmbH., will be further illustrated in the following pages.

Fatty alcohols and primary alkyl sulfates in pharmacology and in the cosmetic industry

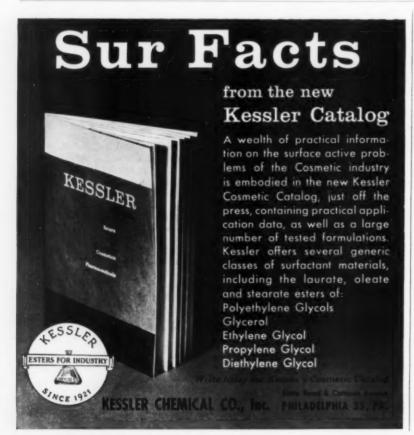
The exhaustive research in the laboratories of the Deutsche Hydrierwerke GmbH. led to the discovery, that fatty alcohols htemselves, with their terminal hydroxyl group, in addition to their use in technology, represent also an ideal basic material for ointments and cosmetic emulsions. Pharmaceutical and clinical research proved the homologues C₁₆ and C₁₈ to be those, which are best tolerated by the skin, and as far as technology is concerned, they are indifferent, and easily emulsifiable. On account of their neutral character, they can be well mixed and combined with other common fatty sub-

stances, and they are also compatible with practically all pharmaceutical catalysts. The most important trade product of this kind is Dehydag Wax O.

The part of oil found within the cranium of the sperm whale is an ester of the oleic acid, which is used in a refined form as Cetiol V® in ointments, creams, and liquid emulsions. This product is also used in oily preparation of lipoide-soluble pharmaceutical products, because, besides being exceedingly well tolerated by the skin, it also possesses a great effectiveness in depth and and outstanding solubility.

The outstanding foaming capacity and the excellent emulsifying quality of primary alkyl sulfates, their great cleansing power in neutral and acid reactions, their capacity to reduce surface tension of water and thus provide the aqueous preparations with a greater extension and a deeper penetration, is utilized in the manufacture of oil-in-water emulsions in the pharmaceutical and cosmetic fields. Sulfates with the base of cetylic or stearylic alcohol, are especially well suited for this purpose. They develop less foam, but on the other hand they are excellent emulsifiers, and they are valued above all in the manufacture of pharmaceutical ointments, emulsions, and cosmetic creams, because they are well tolerated by the skin, and also due to their neutral reaction.

Dehydag Wax N is a basic material from C₁₆ and C₁₈ alcohols with addition of such sodium alkyl sulfates. It is a finished foundation for ointments, creams, and emulsions, for preparations of the type oil-in-water. With Dehydag Wax N it is possible to manufacture preparations in whatever degree of consistency required, from a linament to a tough paste. Dehydag Wax N can be combined with most of the fatty substances commonly



Trade Literature

An informative new booklet just released by Crown Industrial Products Co. contains detailed information on the history of aerosol spray products and their industrial applications today. The 16-page booklet is profusely illustrated with drawings and photographs. Among the subjects covered are the history of aerosol packaging, development of pressure containers and valves, methods of filling and principles of operation. A thorough discussion of cost-saving and timesaving advantages of this type of packaging for industrial and commercial use is also presented.

Techniques for making accurate pH measurements in usually troublesome samples such as soils, emulsions, suspensions and oils are covered in a new data sheet issued by the Applications laboratories of Beckman/Scientific and Process Instruments Division. Proper care of pH electrodes is discussed and step-by-step procedures detailed for pH measurements in dry, porous samples, oils and other water insoluable liquids, slurries, sludges, and viscous, colloidal and highly concentrated samples.

used in pharmacological and cosmetic fields. It is also compatible with practically all of the pharmaceutical biocatalysts.

The structure of Emulgade F® is similar to that of Dehydag Wax N. It contains in addition a certain amount of nonionic emulsifiers. Emulgade F® is especially suitable for the manufacture of thin emulsions, such as cosmetic skin lotion, and in such pharmaceutical cases, when specific emulsion-resistant substances have to be added to the preparation.

Cosmetic skin lotion: Emulgade F® 2,0 Cetiol V® 3,0 Glycerin 3,0 Water 92,0

100.0

The introduction of primary alkyl sulfates into therapy as emulsifiers of a new type, adds a new method of galenic preparation to thetype water-in-oil with a lanolin base. This provides first of all the dermatologist with new means for treatment of skin diseases, since it is now possible to choose the best form of application in each case of sickness. Dehydag Wax, due to its oil-inwater type, is a valuable addition to ointment foundations, which are at present commonly in use.

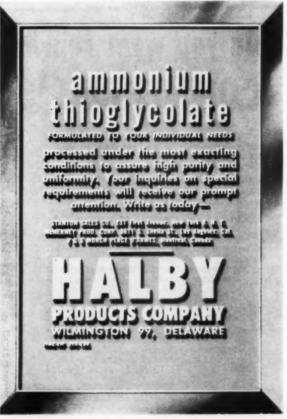
The advantage of the type oil-in-water consists generally speaking first of all in the fact, that biocatalysts, which are soluble in water, are present in true solution in the outside phase, and can be brought quickly to the desired point of action, where they achieve a fast resorption. Due to the wetting effect of alkyl sulfates, which are active on the surface, the water penetrates deep into the folds of the skin and of the mucous membranes, and increases the permeability of mucous mem-

branes, as far as the biocatalysts are concerned. And, because of this improved resorption, it is often possible to reduce the concentration of biocatalysts in preparations to a considerable degree. A fine example of such a possibility is boric acid ointment. The unct. acidi borici, if prepared as prescribed by the Deutsches Arzneibuch (German pharmacopoeia), 6th edition, is a 10% trituration with a white petrolatum base. The resorption of boric acid, which is contained here in undissolved form, can only take place slowly and to a small degree from a fatty skin-alien foundation. In contrast, boric acid ointment with a Dehydag Wax base, with boric acid present in true solution, has a similar or even stronger effect, while containing only 2% of boric acid. According to most recent research, this content can be reduced even further.

This possibility of a general reduction in the amounts of biocatalysts is not only profitable, but there is also less danger of intoxication from overdosage. Since in this type of emulsions water is found in the outside phase, these products can be diluted with water according to needs. The fact, that such ointments can be easily rinsed away, makes them especially suitable for parts of the body covered with hair, as well as in infant care. It is of further advantage, that, in applying fatty substances well tolerated by the skin, less heat is accumulated, than is the case with mineral fats. In addition, when types of oil-in-water are applied to the skin, an evaporation process sets in, which creates in turn a cooling effect, especially valuable in skin diseases with itching sensations.

The positive experience gained in therapy through use of fatty alcohols and alkyl sulfates, has resulted in the inclusion of these substances in recent revised edi-





tions of pharmacopoeiae in many countries.

Especially suited for shampoos are products from dodecylic and tetradecylic alcohols, since solubility, as well as cleansing and foaming qualities are of prime importance for temperatures, at which hair cleansing preparations are used—as was shown in the beginning of this presentation. Such products are available to the cosmetic industry in liquid form, as clear and emulsionlike shampoo bases, and also in paste or powder form (Texapon®). According to the intended use and application they can be mass produced with appropriate additives.

Liquid emulsion-like shampoo with pearly shine and egg additive:

Texapon BS®	98.0
Egg yolk	1.0
Perfume	1.0
	100.0

ca. 22% surface active ingredients, viscosity ca. 25000-

Shampoo in powder form: Texapon Z high conc. 40.0 Sodium sulfate Citric acid 0.2 Perfume 1.0

100.0

ca. 35% surface active ingredients

Alkyl sulfates, especially polyether sulfates, are highly suitable for foam baths. The following formula is an example of such a mass produced preparation, with the

addition of an agent, which stabilizes the foaming action and revives the oversaturation with fatty acids.

Foam bath:	Sodium alginate	1.2
	Glycerin	20.0
	Texapon L 100®	1.0
	Peppermint oil	2.0
	Paraffin oil	2.0
	Chalk	45.0
	Water	29.3
		100.0

Summary:

Among modern surface active agents primary alkyl sulfates are even today of quite great importance.

The variations in their main characteristics through changes in the length of their chain of carbon atoms has been described.

The possible uses of these alkyl sulfates and of fatty alcohol foundations in the cosmetic industry and in pharmacology have been explained.

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CATIONICS IN Cormetics

P. L. DUBROW*

Paul I. DuBrow is section head of the Application Research Laboratory, Chemical Division, Armour & Co. All of his experience has been in fatty acid derivative chemistry. He headed organic research in the Central Research Group and also in the Chemical Division. He was graduated from the College of the City of New York and did graduate work in organic chemistry at the University of Wisconsin. He has been with Armour & Co. since 1943.



he cosmetic industry is a lusty, growing, one-billion dollar a year segment of our economy. It involves the utilization of dozens of chemicals and chemical byproducts. Many of these have been favorite "standbys" since men and women first became concerned with personal hygiene and with attracting members of the opposite sex.

Among the more recently introduced ingredients in cosmetic preparations, however, is a class of compounds known as the cationics. An outline of their physical, chemical and physiological properties in cosmetic formulations seems in order. Perhaps it may provide the needed clue that will solve some chemist's perplexing problem.

Two general areas will be covered: the cationics as chemicals and specific, known applications for these materials, accompanied by selected, published formulations.

Cationics, by definition, are those chemicals which ionize in solution so that the long-chain containing moiety is positively charged. Under an imposed electric force they will act as true cations and migrate to the cathode, the negatively charged electrode. They represent, therefore, a class of surface active chemicals which is the reverse of the negatively charged anionics (the soaps, sulfates, sulfonates, etc.). They have, in fact, been sometimes known as "invert" soaps. As such, they tend to reduce interfacial surface tension and influence wetting action, dispersion, penetration and solubility of solvent systems.

Ionization of Cationics vs. Anionics

RNH2 + H2O → RNH3+ + OH-RCOONa → RCOO- + Na+ soap

 $R_4N : X \rightarrow R_4N^+ + X^$ quaternary ammonium

ROSO₃Na → ROSO₃ + Na+ alkyl sulfate

Long known in organic chemistry, the long chain cationics came to the fore, industrially, about 1935 with the discovery of the high germicidal activity of the completely alkylated products, the quaternary ammonium salts. This latter group will mainly concern us here, since it represents the bulk of the cationics in use today in the cosmetic industry. Introduced originally for their high germicidal activity, the cationics now function also by virtue of other properties inherent in this interesting class of compounds.

The cationics can be excellent emulsifiers, although relatively poor detergents. Combination with nonionics is common for acceptable cleaning action. They can be very active and potent germicidal agents; they can complex and bind moisture and act as effective antistats; they can be good wetting agents, although generally poorer than the anionics or nonionics; they will react with and can be inactivated by protein, some polyvalent ions and most anionics, although structural modifications and certain additives can help markedly; and above all, they exhibit the unique property of substantivity.

This latter attribute, which is not exhibited by the nonionics and only seldom by the anionics, allows for

^{*}Chemical Division, Armour and Co.



It answers a prayer, A snap to dissolve, Yet stays on the hair.

The SOLULANS are liquid, water-soluble lanolin derivatives, and much more! They form persistent emollient films which resist washing away. We have obtained this remarkable effect by giving these compounds a hydrophobic toe-hold in the shape of acetyl groups.

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The SOLULANS are completely soluble in alcohol and in water, and are powerful solubilizers for preparing water solutions of many insoluble substances such as perfumes, antiseptics, dyes, oils and pharmaceuticals.

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Topical pharmaceuticals
Aerosols
Gels and sticks
Anti-perspirants
Deodorants
Body rubs

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attraction to and bonding onto certain surfaces at liquid-solid interfaces. Thus the cationics, as positively charged particles, will deposit from solution on negatively charged surfaces, which include wood, minerals, glass, metals, skin, hair, etc. Rate and extent of this substantivity, or deposition, will be a function of the equilibrium between the attracting and bonding force of the substrate and the tendency toward desorption and resolubilization of the cationic. This, obviously, is a function of chemical structure and a look at these materials from this standpoint is in order (See Table 1).

A demonstration of this effect can be seen in the following photographs. A suspension of Arquad 2HT gives the hazy solution to the left-hand picture; removal of the suspended quaternary ammonium salt by deposition onto the cloth results in the clear solu-

tion shown on the right.





As for physical form, the cationics can be completley water soluble or oil soluble, depending upon the nature of the substituent groups around the nitrogen. The higher the hydrocarbon content, the greater the oil solubility generally. They can vary from crystalline solids to gels and pourable liquids. Decomposition points range from 75° C. to 150° C. (the hydroxides generally decompose when rendered solvent free): compatibility is excellent with the non-ionics (which can supply detergency) and may be with hard waters. They react ionically, in solution, like inorganic salts, ionize completely at low dilutions and are relatively strong bases (the amines displace ammonia from solution; the quaternary hydroxides exhibit a pH as high as sodium hydroxide). They can accelerate or slow metal corrosion, are potent antistats and, of the three classes of surface-active agents, are probably the most irritating and toxic, although this must be related to specific structure.

LD-50's for the cationics can range from 25 mg/kg to >2000 mg/kg and they can show eye irritation effects from far less than 1% to 10% concentrations. Generally, however, at normal use levels (0.1 - 1.0%)

skin and eye irritation are negligible.

The cationics demonstrate a high order of bacteriostatic and bactericidal activity, against a broad range of gram (+), gram (-) and fungus organisms, over a wide pH range. The mechanism, although still a postulate, supposedly involves surface adsorption and interference with the enzyme system of the organism. Chain length, substrate, organism, etc. must be

General Quaternary Formum and Class Name	Typical Trade Names	Supplier	Outstanding Characteristics
(A) CH ₃ 7 ⁺	Arquads Monoalkyl Dialkyl	Armour & Co. Chemical Div.	High germicidal activity. Oil soluble, high substantivity
R-N-CH ₂ X	Catol 2	Am. Cyanamid	on soluble, high substantivity
B'	Cetab	Rhodes Chem. Co.	- Low toxicity - used in mouth
Alkyl (or Dialkyl)			washes — powder.
Tri (or Di-) Methyl	Fixacol Tetrosan	Ciba	- Acid and alkali stable.
Ammonium Salt		Onyx Chem.	Acid and aikan stable.
Г сн₃]÷	Ammonyx T Onyx BTC	Onyx Chem.	
R-N-CH ₂	Triton X-400	Rohm & Haas	Cosmetic Grade — used in Cream Hair rinses.
CH ₃	Zephirol Roccal	W. Stearns	Very common product — good bactericide — high toxicity and
Alkyl Dimethyl Benzyl	Octab Decab	Rhodes Chem. Co.	eye irritation.
Ammonium Salt			
n)	Cetol	Fine Organics	
	Lissolamine A	Imperial Chem.	Acid and Calcium Salt Stable — Powder.
R X	Ceepryn	W. S. Merrill	Wide bactericidal range.
СН	Isothan Q14	Onyx Chem.	Effective against dandruff
Alkyl Pyridinium	Quatresine	Onyx Chem.	associated organism.
(or Morpholinium, Picolinium, Quinolinium, etc.)	G-271	Atlas Powder	Good anionic compatibility. Wide range bactericide.
Ammonium Salt			
CH2 H CH2 H H		\mathbf{x}	
CH ₃ H CH ₃ H H CH ₃ - C - C - C O - C - C O CH ₃ H CH ₃ H H Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt		Rohm & Haas Rohm & Haas Rohm & Haas	 High germicidal activity In solution or solid. Low toxicity — anti-mildew, deodorant, disinfectant.
CH ₃ H CH ₂ H H CH ₃ - C - C - C CH ₃ H CH ₂ H H Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt ("Hyamine Type")	H H H H Hyamine 1622 Hyamine 10-X	Rohm & Haas	In solution or solid.
CH ₃ H CH ₂ H H CH ₃ C - C - C O CH ₃ H CH ₁ H H Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt ("Hyamine Type")	H H H H Hyamine 1622 Hyamine 10-X	Rohm & Haas	In solution or solid. Low toxicity — anti-mildew,
CH ₂ H CH ₂ CH ₃ - C - C - C O C - C O C C - C O C C C C	H H H Hyamine 1622 Hyamine 10-X Triton X-200 Miranol OH	Rohm & Haas Rohm & Haas Miranol Corp.	In solution or solid. Low toxicity — anti-mildew, deodorant, disinfectant. Excellent foamer — low eye irritation — low toxicity.
CH ₂ H CH ₂ CH ₃ H CH ₂ CH ₃ C C C C CH ₃ H CH ₁ Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt ("Hyamine Type") E) N - CH ₂ R - C CH ₂ N CH ₂ CH ₂ ONa CH ₂ COONa Sodium-1-(β-Hydroxyethyl)- 1-(Carboxymethyl)-2-(Alkyl)-	H H H Hyamine 1622 Hyamine 10-X Triton X-200 Miranol OH	Rohm & Haas Rohm & Haas	In solution or solid. Low toxicity — anti-mildew, deodorant, disinfectant. — Excellent foamer — low eye
CH ₃ H CH ₂ CH ₃ H CH ₂ H H CH ₃ C C C C CH ₃ H CH ₂ H H Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt ("Hyamine Type") E) N CH ₂ R C CH ₂ N CH ₂ COONa Sodium-1-(β-Hydroxyethyl)- 1-(Carboxymethyl)-2-(Alkyl)- 2-Imidazolinium Ammonium Salt. F) H O H H H N C C C N C C C OOCR H H H H N (Acyl Colamino Formyl methyl) Pyridinium Ammonium Salt. G)	H H H Hyamine 1622 Hyamine 10-X Triton X-200 Miranol OH	Rohm & Haas Rohm & Haas Miranol Corp.	In solution or solid. Low toxicity — anti-mildew, deodorant, disinfectant. — Excellent foamer — low eye irritation — low toxicity. — Non-irritating — low oral toxicity — good bactericide — good
CH ₂ H CH ₂ CH ₃ H CH ₂ CH ₃ H CH ₂ H H Diisobutyl (p - t - Octyl) Phenoxy Ethoxy Ethyl Dimethyl Benzyl Ammonium Salt ("Hyamine Type") E) N - CH ₂ R - C CH ₂ N CH ₂ CH ₂ ONa CH ₂ COONa Sodium-1 - (β-Hydroxyethyl)- 1-(Carboxymethyl)-2-(Alkyl)- 2-Imidazolinium Ammonium Salt. F) H O H H H N - C - C - N - C - C - OOCR H H H N - (Acyl Colamino Formyl methyl) Pyridinium Ammonium Salt.	H H H Hyamine 1622 Hyamine 10-X Triton X-200 Miranol OH Emcol E-607 X	Rohm & Haas Rohm & Haas Miranol Corp. Emulsol Corp.	In solution or solid. Low toxicity — anti-mildew, deodorant, disinfectant. Excellent foamer — low eye irritation — low toxicity. Non-irritating — low oral toxicity — good bactericide — good hair retention — pH 5 — 5.5. Highly soluble — good foamer in 0.1% soln.; good bactericide — used in cold creams, sham-



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ACETULAN is composed of acetylated lanolin alcohols prepared by an exclusive process. It is soluble in alcohol, propellants, and in most oils. It acts as a solubilizer and plasticizer for many substances which are used in aerosols, emulsions, lotions, and make-up.

ACETULAN is hypo-allergenic and non-irritating.

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Aerosols Emulsions Shampoos Powders, talcs Nail polish removers Sun tan oils

Ointments and lotions Rouge and lipsticks Liquid make-up Baby products Hair preparations Shaving preparations

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considered before an effective "in situ" working level can be established. Bactericidal activity at solution levels of one part in several hundred thousand against S. aureus, for example, have been claimed, while bacteriostatic action can be exhibited at even lower levels. Quaternary ammonium salts containing two long chains generally show a lower order of activity than those with one chain but are less toxic; addition of ethylene oxide will reduce bactericidal effect, although solubility in polar solvents will increase; chlorinated aromatic substituents increase activity, etc.

Although cationics, as a class, will include the amines (primary, secondary, tertiary, cyclic, aliphatic, aromatic, etc.) and their salts, our major concern in a cosmetic frame of reference is with the quaternary ammonium compounds. These are pentavalent introgencontaining compounds, of the general formula:

$$\begin{bmatrix} R_1 \\ R_2 - N \\ R_3 \end{bmatrix}$$
 $\begin{bmatrix} X^- \\ X^- \end{bmatrix}$, where the R groups may be

any organic chain, at least one of which should be a long chain, to give the proper hydrophobic-hydrophilic balance for surface activity. The R's may be alkyl, aryl, cyclic or heterocyclic, alike or dissimilar, while the truly ionic X-may be any anion, although generally halide or alkyl sulfate.

Such chemicals are currently being produced as standard products by many industrial concerns, but certain common classes can be recognized from the welter of those synthesized in the laboratory. A resumé of these seems in order at this point. Structure, trade names, suppliers and outstanding properties will be included when possible, with particular reference to those that have already found a place in the cosmetic industry.

The quaternary ammonium salts are prepared by direct alkylation of the precursor, primary, secondary or tertiary amines, with or without solvent. Most are in the \$.50 - 1.00/lb. (active) price range, marking them as specialty chemicals. Use concentrations, however, are generally so low that additive cost is often negli-

As for the general areas of industrial application of the cationics, they range from ore flotation to fabric softening, starch solution viscosity stabilization, asphalt anti-stripping, pigment dispersion, emulsion paint freeze-thaw stabilization, sludge inhibition in fuel oils, corrosion inhibition, wax, silicone and oil emulsification, metal-drawing lubrication, bactericides, heavy metal extractants, anticaking agents, etc.

Two properties, however, have accounted for their use in cosmetic formulations, from a personal hygiene and a purely cosmetic standpoint. These are their substantivity and their bactericidal characteristics.

Obviously, any product that can be applied and used at the normal skin pH, that can be adsorbed onto skin or hair and can modify those surfaces is of interest to the cosmetic chemist. When these modifications can contribute destruction of undesirable organisms, antistatic activity and increased softness and manageability of skin and hair, that interest is essential to the creator of new and more versatile preparations. And the list of applications already tried is a broad one, including anti-perspirants and deodorant formulations, hair rinses and lotions, hand and emollient creams and lotions, mouthwashes, antiseptic lotions, depilatories, baby toiletries, etc. Incorporation into aerosol formulation, if desired, is easily accomplished,

although can corrosion should be checked.

But what of the specifics? Where have these chemicals played a part in cosmetic formulations, what do they contribute and where, perhaps, can they play a greater role? This can best be done by indicating where they are used, at present, in certain known applications and by reproducing certain representative formulations.

[One word of caution to the experimental chemist. The problem of compatibility with other ingredients must always be borne in mind in evaluating the specific effect of the added cationic. Certain standard products, colors, peppermint oils, boric acid, citric acid, etc., as well as polyvalent ions should be suspect, while combinations with anionics should generally be avoided.]

Formulations have been taken from Sagarin's "Cosmetics" (Interscience—1957). Page references to for-

mulas used and indicated will be listed.

One major area of application is in skin care formulations, particularly in the so-called emollient creams and lotions. Using cationics as emulsifiers for mineral oil, lanolin, etc. (with or without nonionics) allows for a rapid break on contacting the skin (the cationic emulsifier plates out and allows the emulsion to break) and an intimate and fast deposition of the emulsified components. Since the cationics themselves can be skin softeners and germicides, certain reinforcing effects and potential plus values are predictable. Such preparations can also function, possibly, as humectants and antistats, because of their ability to bind and retain moisture.

Some talk has also been current as to the use of so-called barrier agents for hands. Perhaps a product such as Arquad 2HT, at moderate concentrations, can

act as a moisture repellent and protectant.

Three typical formulations are shown below:

Emollient Cream O/W Cationic Type

(pg. 123)	
Isopropyl Palmitate	15.0%
Peanut Oil	9.0
Light Mineral Oil	10.0
Petrolatum	5.0
Beeswax	15.0
Propyl Paraben	0.15
Antioxidant	0.05
Methyl Paraben	0.15
Glycerol	5.0
Hyamine 1622	1.0
Water	39.3
Perfume	0.35

Emollient Lotion
O/W Cationic-Nonionic Type

(pg. 137)	
Lanolin	2.0%
Light Mineral Oil	2.0
Tegin	6.0
Propyl Paraben	0.15
Methyl Paraben	0.15
Sorbitol	2.0
Cetyl Trimethyl Ammonium Bromide (Lissolamine V)	0.16
Water	87.24
Perfume	0.3

Hand Cream Cationic-Nonionic

	(bg. 110)	
Glycerol	Monostearate	10%
Lanolin		2.0

Stearyl Colamino Formyl Methyl	
Pyrodinium Chloride (Emulsept)	1.5
Glycerol	15.0
Methyl Paraben	0.1
Water	71.4
Perfume	q.s.
Color	q.s.

In addition, typical formulations for other quaternary ammonium salts can be found as follows:

Emollient Creams—O/W—Cationic Pg. 123
Emollient Creams—W/O—Cationic Pg. 124-5
Emollient Creams—W/O—Cationic-Nonionic Pg. 125-5
Emollient Creams—W/O—Cationic-Nonionic Pg. 125-6
Emollient Lotions—O/W—Cationic Pg. 137
Emollient Lotions—O/W—Cationic Pg. 137
Emollient Lotions—O/W—Cationic Pg. 137
Hand Creams—Cationic-Nonionic Pg. 173
Hand Creams—Cationic—Anionic Pg. 173
Hand Lotions—Cationic-Nonionic Pg. 176
Hand Lotions—Cationic-Anionic Pg. 176

Mouthwashes are another obvious place for the cationics, in view of their high germicidal activity. (After-taste and in-situ activity should be carefully checked here). Apart from the obvious medicinal function of keeping harmful organisms in check, the quaternary ammonium salts act as mouth deodorants, while some evidence of reduction in tooth decay has been noted. From a dental hygiene standpoint, they have been used to control such troublesome diseases as glossitis, gingivitis, dental sore mouth, etc.

A typical mouthwash formulation follow	ws: (pg. 374)
Cetyl pyridinium chloride (Ceepryn)	
Sorbitol (70% solution)	20.0
Cinnamon Oil	0.05
Peppermint Oil	0.10
Citric Acid	0.10
F.D. & C. Red. #2	0.001
Tween 60	0.30
Ethyl Alcohol	10.0
Water	69.34

The whole field of hair rinses and shampoos is a very fertile and promising one for the cationics. Here again, their germicidal properties help in controlling scalp infections, particularly those associated with Dandruff.

But the prime requisite for a hair gromer is manageability and softness and the cationics are quite effective in this area. They are generally incorporated with nonionics, for a cleansing combination, but their potential as after-rinses should not be overlooked. Here, compatibility with carryover anionics can be a problem, although additives to eliminate this possibility are experimentally available.

In addition, they can perhaps act as moisturizing agents, can contribute emollient and antistatic prop-

erties and non-greasy "slip" to the hair.

The cationics have been formulated into shaving lotions, for softening of the beard and for antiseptic purposes; in cuticle preparations, again mainly for their bactericidal contributions.

But a more common approach is their incorporation in deodorant preparations, where their marked substantivity reduces loss by sweating and so allows for long time, effective control of undesirable organism produced by-products.

Formulation into high talc-containing, solid materials is probably ineffective, since quaternary adsorption onto the talc will reduce effective cationic levels.

The last major area to be considered is in baby toiletries. Here, they have been markedly effective in controlling hospital impetigo outbreaks and in contributing to the skin care of new born and young babies.



From the castor bean, A lanolin ester Fit for a queen.

The RICILANS are 100% active, unsaturated polymeric derivatives of lanolin and castor oil. They are classed as true liquid waxes. The RICILANS are exceedingly stable, almost adorless viscous hydroxyesters which have balanced hydrophilic and hydrophobic groups. An acetylated form is available (Ricilan C) with increased hydrophobic characteristics. These unique products were developed by our Research Laboratories to provide cosmetic chemists with completely new tools for cosmetic research and formulation.

The RICILANS are unusual emollients, penetrants and spreading agents. They dissolve, plasticize and solubilize most cosmetic raw materials. We recommend that they be used in lipsticks for emollience, gloss, and color enhancement; in aerosols for the emollient films they impart; and in creams, lotions, and hair preparations for the unusual soft, waxy after-feel left on skin and hair.

Write today on your letterhead for technical literature and samples.



American Cholesterol Products

AMERCHOL PARK - EDISON, N. J.

No history of skin irritation has been noted, while intimate skin contact and low urine removal have eliminated diaper rash by elimination of ammonia producers and bacterial induced skin irritation. Combined with cationic treated diapers, very effective controls can be obtained.

Use of the quaternary ammonium salts, incidentally, as diaper cloth softeners (Arquad 2HT, for example) also reduces mechanical chafing, an added plus value.

Use of the Miranols in baby shampoos has also been claimed, with extremely low eye irritation effects.

Incorporation into creams, lotions and oils is possible. A reference listing of certain random cationic formulations should be noted, including:

After-shave lotion	pg. 449, 452
Peroxide Hair Rinse	pg. 483
Cuticle Softener	pg. 707
Aerosol Deodorant	pg. 827
Baby Powder	pg. 870

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Greater Sales of Hair Sprays

Hair spray is a fairly established product and one that has made some remarkable strides. From a standing start in less than ten years hair sprays have advanced to the lead position as the number one best selling aerosol spray product. In 1957 it is estimated that more than 90 million units were produced with a retail sales value in excess of 80 million dollars. Yet according to surveys only about half the women of America use hair spray.

To avoid complacency from the foregoing nearly half the users of hair spray have something they dislike. The biggest dislikes are that it makes hair stiff, hard or unnatural looking—that it makes the hair sticky, gummy, difficult to comb or that it has too strong or lasting a scent.

Is price a factor in the purchase of a hair spray? According to a survey of E. I. duPont de Nemours & Co. Kinetic Chemicals Division, 60% of the users said that price has no influence on the purchase of a hair spray.

Let's take a look at what non-users have to say about hair spray. Of the 69% who had tried a hair spray at one time or another three quarters had tried only one brand. Perhaps this group is worth trying to sell again with some of the newer type of hair spray, because, when asked what qualities would be needed in a hair spray, to get them to try it again, they mentioned almost to a woman that a hair spray must be soft, natural and invisible.

From the foregoing it seems apparent that the large potential market of non-users of hair spray will not be converted simply by increasing advertising expenditures. What also is needed, if we have analyzed the survey properly, is more product research toward improving the qualities that women want in a hair spray-that is a hair spray that is soft, natural looking, invisible and does not leave the hair gummy, sticky or set looking. Maybe some manufacturers have such a product in their laboratories now or even in the first stages of marketing. If so, the women of America are waiting for your product. If you sell them effectively through advertising and all other forms of communication it should be relatively easy to increase the current penetration figure of 44% to near the saturation level .- Abstract of T. G. A. address by Howard Trumbull.









Offices and Plant: 3618 Oceanside Rd. Oceanside, N. Y.

Showrooms: Empire State Bldg., 350 5th Ave., N. Y., N. Y.







1-PARFUMS CIRO

Parfums Ciro has added to its line of Continuities, Savon de Ciro, a French milled soap in the colors and fragrances of their six perfumes: Danger, Reflexions, Surrender, New Horizons, Doux Jasmin and Ricochet. The large package in a white and gold box contains 6 cakes, one of each fragrance and color. It retails at \$4.50. The smaller package is available in each fragrance and color, 3 cakes to a box to retail at \$2.50.

2-GUERLAIN

As a special gift to a couple, the new "Gift for Two" from the House of Guerlain combines in one compact package, a bottle of Shalimar Cologne for her and a bottle of Extra Dry Cologne for him. These matching, square, crystal-clear bottles contain three ounces each. They have leak-proof gold-finished caps, Retail price is \$8.00 plus tax.

3-LENTHERIC

To give point-of-purchase impetus to the Fall fashion-fragrance promotion, Lentheric has created a unique eyecatching display stand. Featuring a free form gold wire oak leaf set above a shelf supported by four slender wire legs, the stand offers an exciting background display for the Tweed fragrance preparations. The oak leaf, filled in on the left side with the Tweed-textured paper, reveals the theme of the promotion "Wonderful Things Happen When You Wear Tweed" in a sign which cuts across the open right side of the leaf. The shelf, which looks like grained wood, offers display space for four or five items. Additional packages may be grouped around the stand.

4-BURMA VITA CO.

For years the aerosol industry has been trying to discourage the use of the word "Bomb" in reference to consumer aerosols. In an apparent attempt to cash in on the American male's response to the word "Bomb" at the point of pur-







chase, Burma Vita Co. has introduced a new shaving cream for men, "Burma Shave Metholated Shave Cream Bomb," as the newest item in the firm's line of men's toiletries. The new dispenser has green lettering on the yellow can.

5—SHULTON

Shulton, Inc., has designed this colorful 3-dimensional counter unit to display its spray cologne foursome: Desert Flower, Escapade, Early American Old Spice and Friendship Garden. Vacuum-formed plastic replicas of the bottles, with each fragrance in its own pastel shade, are set on background panels of black and white. The oval top piece is pink, blue and gold.

6-KATHLEEN MARY QUINLAN

A new, matching, three piece set, consisting of a refillable, lipstick, a compact and an eye shadow container, has been produced by the Scovill Manufacturing Co., for Kathleen Mary Quinlan, a wholly owned subsidiary of Dagett & Ramsdell, Inc. Each of the three containers is finished in a combination of frosty and polished silver plate. On the dome top of the lipstick and on the cover of the compact appears the Kathleen Mary Quinlan crest.

7-HOUBIGANT

For Fall and Christmas selling, Houbigant has packaged its Chantilly Liquid Skin Sachet in a festive lantern that can be hung on a tree. Retail price is \$2.00. This special display unit, a replica of a lantern, holds twenty-four pieces of merchandise, sixteen of which stand on the unit, the balance for loose display on the counter.

8-MENNEN

Mennen Baby Products, as a special introductory offer for their New Baby Powder, will offer a free trial package of "Q-Tips" cotton swabs with the purchase of a 59¢ container of the powder. "Q-Tips" offer includes a free trial can of New Mennen Baby Powder with the purchase of the 59¢ and 98¢ packages of "Q-Tips." Both companies will advertise the tie-in promotion.









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menting all that is current for the pages of our publication.

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JANUARY '59 IS THE ISSUE.

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News

and Events

S.C.C. Flying Trip to Five European Countries

Members of the Society of Cosmetic Chemists flew from Idlewild airport Sept. 5 to tour Italy, Germany, Denmark, Holland and Belgium. They returned September 29.

While in Bonn, Germany, the group attended the first technical meeting of the newly formed Society of German Cosmetic Chemists. The two day seminar included papers on the chemistry of hair cosmetics, emulsions and the bio-chemistry of perfumes and cosmetic ingredients.

The group also attended the second meeting of the International Congress of Cosmetic Chemists. The groundwork for the formation of an International Congress was laid during the 1957 tour with the purpose of gaining universal recognition for the cosmetic chemist as a scientist and for the science of cosmetics. In Italy the group and Dr. Robert Mariott of the S. C. C. of Great Britain visited the plant of Esperis S. A. in Milan. Their attention was chiefly centered on the high pressure hydrogenation department where 100% hydrogenated lanolin is manufactured. Much interest was taken

also in the new laboratory for the creation of modern cosmetics. An excursion was also made to Rome. The stay in Germany included a trip on the Rhine from Bonn to Bingen.

The group then flew to Copenhagen for sightseeing and then to Amsterdam Holland. The last stop was at Brussels where the Worlds Fair was visited.

Kolma: Laboratories Research Center Now in Germany

Based on a survey of over a year, Kolmar Laboratories Inc. located its research center in Wiesbaden, Germany, last month. The center will concentrate on basic research. Vice President Dr. Jacobi, an authority on all phases of cosmetics, is the director of the research center and has on his staff three Ph.D's, a physician, an histologist and a corps of chemists.

Applied research has been a factor in the growth of Kolmar Laboratories in the past 37 years. Under the direction of Michael Spinapolice, vice president in charge of product development, numerous successful products have been developed. In Milwaukee, Charles Kircher, vice president in charge of lipstick and related product research has also made

many contributions to the development of the company's products. In foreign countries where Kolmar has successful operations such as France, England, Germany and Australia, independent research is carried on. The headquarters of Kolmar Europe are in Paris, France.



W. J. Wick, president of Kolmar Laboratories has moved his headquarters to Port Jervis, N. Y. because of the concentration of the cosmetic industry in the East. Vice President and Controller G. J. Entringer also moved to Port Jervis. Since September 1 the executive offices of the company have been in Port Jervis. William Buth, vice president of Wicken Products, the company's chemical division, is also now located in Port Jervis, where he will head up a new division of Kolmar research.

Lessing L. Kole, chairman of the board and founder of the company will carry on in Milwaukee, Wisc.



Members of the Second S.C.C. European Tour Pose before the Take-off at Idlewild Airport. Conferences were held in Five Countries

Philadelphia Beautyrama Draws Record Crowds



Enhanced by showings of Dior originals twice daily, The Philadelphia Inquirer's second annual presentation of BEAUTYRAMA, America's major cosmetic fair for consumers, attracted overflowing crowds to the ballroom of the Sheraton Hotel. The clamor for glamour necessitated the curtailment of ticket sales several times during the three-day exhibit that ended September 5. The combined display of beauty aids and costumes proved an irresistible lure to 10,461 visitors, 25% over the 1957 attendance.

NBBMA Directors to Meet in New York December 2

The board of directors of the Nattional Beauty and Barber Manufacturers' Assn. will meet in the Advertising Club, New York City on the evening of December 2.

A clever promotion for the forthcoming convention at the Hotel Concord, Kiamesha, N. Y. called the "NBBMA Convention Flash", issued at intervals, emphasizes the features to be expected at the annual meeting May 21-24, 1959.

Bonne Bell Issues New Blue Book House Organ

Bonne Bell Inc., Cleveland, Ohio has issued the first number of Bonne Bell's Blue Book which contains 12 pages of relevant material of interest to the

There is an article "Teenagers Welcome Help." Bonne Bell introduced teenage beauty assemblies last Spring since which time 200 lectures have been booked and nearly 35,000 questionnaires have been received as entries in a contest. As a result extra prizes had to be offered.

Also in the issue is a story on the Bonne Bell Silver Charm Society. The mark of membership is a charm bracelet with one silver bell charm for each year of service. About 200 selected stores distribute Bonne Bell treatment and makeup preparations.

Graduate Students Of St. Louis **College Visit Plants**

The graduate students in Industrial Pharmacy of the St. Louis College of Pharmacy and Allied Sciences are to have a practical education on the manufacture of pharmaceuticals and drugs as the result of a series of visits to leading plants in the pharmaceutical and cosmetic industries arranged by Prof. C. L. Huyck of the Dept of Industrial Pharmacy of the college. The trips started September 26 to the Cole Chemical Co. In October a visit will be made to the plant of Merck & Co. and each month thereafter until June a visit will be made to other plants.

Directory of Independent Laboratories Issued

The seventh edition, 1958, of the Directory of the American Council of Independent Laboratories Inc. which lists 500 individual services performed by one or more of the leading testing and research laboratories in the U.S., is available on request. Applications should be sent to the Executive Secretary, 4302 East-West Highway, Washington, 14, D.C.

Bronze Placque Honoring His Service Given to Dr. Guenther

An interesting lecture illustrated with color movies, by Dr. Ernest Guenther, vice president and technical director of Fritzsche Brothers Inc. on the production of essential oils in Africa was the feature of the October 15 meeting of the American Society of Perfumers.

A bronze plaque in recognition of his years of achievement in the study of essential oils was presented to Dr. Guenther by the Society.

Jacques A. Mason, president, presided with his usual tact and good humor at the meeting.

Fifth S. C. C. Cosmetic Seminar **Draws Outstanding Chemists**

The fifth annual seminar of the Society of Cosmetic Chemists October 8 and 9 covered biological and clinical aspects of the lipids on the skin, the significance of consumer testing to research and the theory of solubilization. All sessions were held at the Barbizon-Plaza hotel, New York City. Luncheons were held in the New York Academy of Sciences building. Much credit is due to the seminar chairman, Dr. Henry Kreider for the interest-

ing program.

Five papers were presented in the session on Biological and Clinical Aspects of the Skin. These were: "Biochemistry of Sebum," V. R. Wheatley, Dept. of Medicine, University of Chicago; "Acid Number and Spreading Index of the Human Skin Surface Lipids", Leonard Harber, Dept. of Dermatology, New York University Post Graduate Medical School; "Lipid Studies on Stripped and Unstripped Human Skin", Richard Scher, Dept. of Dermatology, New York University Post Graduate Medical School; "Biological and Clinical Features of Sebaceous Excretion", A. M. Kligman, Dept. of Dermatology, School of Medicine, University of Pennsylvania; "The Pathologic Reaction Patters of the Seb-aceous Gland in Experimental Stress," J. S. Strauss, School of Medicine, Boston University. The panel discussion followed with Victor H. Witten, School of Der-matology, New York University Post Graduate Medical School and Dr. Earl O. Butcher, Dept. of Anatomy, College of Dentistry, New York University.

With Edward Sagarin as moderator the Significance of Consumer Testing to Research was considered at the second session. Papers presented were: "Does Product Testing Make Sense?", Henry Brenner, Home Testing Institute; "Selecting Methods of Measurement", Dean Foster, U. S. Testing Laboratories; "Consumer Testing as a Guide to Product Development", Norman Ishler, General Foods Corp. Research Center; and "The Cosmetic Chemists Appraisal of Consumer Research," Mrs. Clare Brown Amabile, Clare Brown Associates.

The Theory of Solubilization was the theme of the only session on the second day of the seminar. Prof. Emery I. Valko, Lowell Technological Institute was moderator. Two papers were presented: "The Solubilization Phenomenon", H. B. Klevens, Mellon Institute and "Micro- Emulsion". Prof. J. H. Schulman, of the Dept. of Chemical Metallurgy, Columbia Uni-

versity.

Trips were made by the members to the plants of Avon Products in Suffern, N. Y.; Helena Rubinstein Inc., Roslyn, Y. and van Ameringen-Haebler, Union Beach, N. J.

Chisholm-Ryder Co. Acquires International Filling Machine

The Chisholm-Ryder Co., Hanover, Pa., has acquired the International Filling Machine Corp., Petersburg, Va. International is one of the largest manufacturers of liquid filling machinery.

Parfums Christian Dior Paris Receives Award for Export Business

Serge Heftler-Louiche, head of Parfums Christian Dior Paris, was recently presented with a special award by Mr. A. Pinay, Minister of Finance in France, for the best export business of the year.

Under the direction of Mr. Heftler-Louiche, the company has experienced an extraordinarily rapid development with production rising from 6 tons in 1950 to 115 tons in 1957. Nearly half of these shipments were exported to a hundred different countries. Between 1951 and 1957 the exported shipments increased by 50% each year over the preceding year.

Mr. Heftler-Louiche credits this rapid rise in large part to the meticulous selection of the company's agents and to the extreme care with which accounts are appointed and supervised in foreign countries.

This recognition of the outstanding export attainment of Parfums Christian Dior Paris is equivalent in the French field of business to winning an Oscar. Mr. Pinay, Minister of Finance, is shown presenting the award to Mr. Heftler-Louiche at an official gathering in Paris.

S.C.C. to Hold Annual Technical Meeting

The annual technical meeting of the Society of Cosmetic Chemists will be held November 20 at the Hotel Statler, New York. The Annual Cocktail Hour and Dinner Dance will be held at 6:30 P.M. at the same hotel.

The tentative program submitted by Richard K. Lehne, the chairman of the program committee follows. Dr. Glen C. Finger, Illinois State Geological Survey, "Notes on Aromatic Fluorine Compounds"; R. J. Meyer and L. Cohen, B. F. Goodrich Chemical Co., "The Rheology of Hydrophilic Polymer Solutions as Related to Suspending Ability"; Robert Goldemberg, Shulton Inc., "Hair Coloring—Modern Formulation Considerations"; Dr. S. G. Knight, University of Wisconsin, "The Therapeutic Potentialities of Triglycerides"; Edward Temple, Plax Corp., "High Density Polyethylene Bottles"; Dr. James Oldshue, Mixing Equipment Co., Inc., "Fluid Mixing of Cosmetic Formulations"; Dr. L. S. Fosdick, Northwestern University, "Theoretical Aspects of Caries Control with Dentifrices and Mouthwashes".

William Hannan Marks 50th Year With Kohnstamm

J. William Hannan, Chicago salesman for H. Kohnstamm & Co., was recently honored on the occasion of his 50th anniversary with the company. The testimonial dinner attended by the executive staff, sales representatives and associates in the Chicago office, was given in his honor at the Conrad Hilton Hotel in Chicago. Robert H. Pulver, executive vice president of the company, presented Mr. Hannan with a 50-year diamond service pin and a substantial check. His associates presented him with a gold wrist watch.

Serge Heftler-Louiche Receives Special Award



Charles L. Teitelbaum Joins Coty Research Laboratories

The appointment of Charles L. Teitelbaum to the perfume research laboratories of Coty, Inc., has been announced by Philip Cortney, president. Mr. Teitelbaum, who won the Frederick Gardner Cottrell Fellowship and Atomic Energy Commission Fellowship, studied at Purdue University where he received his M.S. and Ph.D. degrees. He is a member

of Sigma Xi, Phi Lambda Upsilon and the American Chemical Society. Mr. Teitelbaum has written numerous articles which have appeared in The Journal of the American Chemical Society, American Perfumer and Aromatics, Journal of the Society of Cosmetic Chemists and Journal of Organic Chemistry. Prior to his joining Coty, Inc., Mr. Teitelbaum was associated with the Antibiotics Division of Heydon Chemical Corp. and Battelle Memorial Institute.

Roman Landmarks Promote Simonetta's Incanto Perfume



Paul P. Woolard, Vice President of Simonetta, Inc., and Richard Falcon of Morse International Advertising Agnecy, look over their three-dimensional window display of famous Roman landmarks that will call attention to INCANTO PERFUME by fashion-designer Simonetta of Rome in selected stores throughout the country this Foll. The replicas in precise scale of eight historic monuments . . . the Basilica of St. Peter, Castel Sant'Angelo, the Pantheon, the Imperial Forum, the Coliseum, the Arch of Constantine, the Travi Fountain, and the Spanish Steps . . . were constructed of wood and composition material from hand-carved wood master models. The display . . . five feet wide, fifteen inches high, two and a half feet deep . . . was executed by Bliss Display Corporation.

Polaks Frutal Works Executives Cover the World

For executives of internationallyminded Polak's Frutal Works, Inc., intercontinental travel is part of the job. Maintaining a close personal liaison between its tar-flung offices recently, were these top PFW officials: Bernard Polak. president, left for Manizales, Colombia where he will attend the opening of a subsidiary company, Polak's Frutal Works de Colombia Ltda; J. E. Meihuizen, managing director of PFW's associated firm in Amersfoort, Holland, has arrived in the United States on a two-week visit. He is conferring with PFW officials at their U.S.A. offices in Middletown, N. Y.; PFW's Treasurer, Eric Vles, recently returned from a 19 day trip to Europe. Making the visit with representatives from the Society of Cosmetic Chemists, Mr. Vles' itinerary included Rome, Milan, Bonn, Copenhagen, Amsterdam and Brussels.

Fragrance Foundation Convention October 21 in Waldorf-Astoria

The ninth annual convention of the Fragrance Foundation will be held in the Waldorf-Astoria hotel, New York, October 21. The convention will open with a business meeting for members only. This will be followed by a reception and luncheon open to all after which an open meeting will be held.

Shepherd Elected to Board of Midland Aerosols, Ltd.

H. R. Shepherd, president of Aerosol Techniques, Inc., Bridgeport, Conn., has been elected a director of Midland Aerosols. Ltd., Wolverhampton, England, the largest aerosol company in Europe, Mr. Shepherd was instrumental in establishing the Midland organization five years ago

Geigy Chemical Corp. Celebrates 200th Anniversary

Geigy Chemical Corp. celebrated the firm's 200th anniversary at a dinner dance October 7, in the Sheraton-Astor Hotel for 1,200 employes and their guests.

The main speaker of the evening was Charles E. Koechlin, chairman of the boards of Geigy Chemical Corp. and of J. R. Geigy, S. A. Mr. Koechlin, who started with the Geigy companies in 1908, and who is a direct descendant of the firm's founder, traced the company's development from 1758, when J. R. Geigy opened a small shop in Basel, Switzerland. 200 years later, Geigy has be-come one of the world's major chemical producers with branches and subsidiaries in 86 countries.

Other speeches were made by William F. Zipse, President of Geigy Chemical Corporation, and by Charles A. Suter, Executive Vice-President.

Mr. Zipse, who told of some of the high points of the company's history in

the United States, was hired by Geigy in 1903, the same year the American sub-sidiary was formed. Mr. Zipse pointed out that more than 60 of the company's employees in the United States have more than 25 years of service.

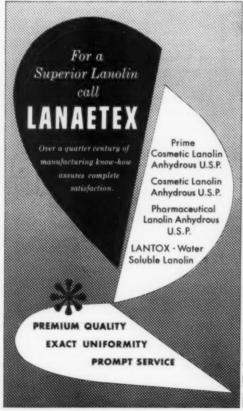
Following the dinner, a 30-minute color film entitled "Paths of Progress" was shown. The film depicts the roles played by the company's many products in the lives of everyone, and gives an intimate view of the operations of the company's plants and laboratories.

The party was the first of a series to be held during October in major centers of the company's activities throughout the United States and Canada. The New York City party was for employees from the company's offices and plants in New York, New Jersey and Pennsylvania.

Other celebrations will be held in Toronto, Canada: Providence, Rhode Island: Charlotte, North Carolina; Mobile, Alabama; San Francisco, California; and Chicago, Illinois. All of the celebrations, like the Astor party, will be family af-

Events in Industry in India Given in Newsletter

To provide a news summary of events taking place in the fields of industrial and general economic development in India, The Embassy of India, Information Service, 2107 Massachusetts Ave., Washington 8, D. C. is issuing a Newsletter. Copies may be had by writing to the Em-



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van Ameringen-Haebler Subsidiary Celebrates Anniversary

van Ameringen-Haebler, Inc. recently marked the 10th anniversary of its subsidiary, van Ameringen-Haebler, S.A.R.L., at a dinner celebration for its employees at Le Grand Veneur in Paris. Attending the function from the parent company were A. L. van Ameringen, board chairman, and Ernest Shiftan, vice president and chief perfumer.

Jacques Weill, managing director of the Paris unit, commented on the expansion of the company and introduced Mr. van Ameringen, who complimented the local organization on the growth and development of its business. He noted the many achievements in research and chemical production pioneered by the parent company, which will celebrate its 50th anniversary next year, and stated that the company will continue to grow as long as its people have the desire for perfection and leadership in product superiority.

van Ameringen-Haebler, S.A.R.L. produces perfume and flavor materials for the soap, cosmetic, fragrance, food, beverage and related industries in Europe and North Africa and also serves American companies who have manufacturing and distribution units in those countries.

Neiman-Marcus Features Yardley in British Products Festival

Yardley of London had exclusive representation in the toiletries field in the Neiman-Marcus "British Fortnight," a store-wide promotion of men's merchandise and services with cultural exhibits and functions during the week of October 12. A focal point of the promotion was the Yardley-sponsored exhibition of British male fashions, past and present, assembled by James Laver, curator of prints of the Victoria and Albert Museum in London.

The Yardley Cavalcade of Fashion, one of the major exhibits during the promotion, traced the history of British supremacy in men's fashions from pre-French revolutionary days to the present. The historical costumes, shown on wire figures against a stark white background, were selected from the Doris Langley Moore collection by James Laver.

'Aerosol Supermarket' To Highlight Tenth Anniversary

To mark the 10th anniversary of the Aerosol Division of the Chemical Specialties Manufacturing Assn., the aerosol industry is staging an "Aerosol Supermarket" reception December 8th, at the Hotel Commodore, New York City, during the 45th annual meeting of the CSMA.

The West Ballroom will be arranged in typical supermarket style with stacks, promotional material and booths displaying the great variety of present-day aerosols of every type. Featured under such familiar supermarket headings as "Household", "Foods", "Drugs", "Cosmetics", "Insecticides" and "Paints", will be many new as well as well-known aerosols which will be donated from several hun-

Dr. and Mrs. Felton Visit Versailles Plant



Dr. and Mrs. Joseph Felton have returned from an extensive European trip. Considerable time was spent conferring with Mr. Leon Gefen and The Felton Chemical Co.'s Versailles plant where the above photo was taken.

dred marketers in the pressure packaging field. This is expected to be the most comprehensive display of presently available aerosol products ever assembled. Experts from the aerosol industry will serve as "sales clerks" in each display area. They will explain how aerosols function, and will demonstrate the latest advances. They will also review the fabulous growth of aerosols.

R. D. Webb & Co., Inc. to Market Coastal Brand Lemon Oil USP

R. D. Webb & Co., Inc. of Cos Cob, Conn. has been appointed official sales agent for Ventura Processors Coastal Brand Lemon Oil USP. The addition of this product enables R. D. Webb to bring its customers an even broader selection of fine California lemon oils.

New Officers of Drug, Chemical & Allied Trades Section of New York Board of Trade Make Plans For Coming Year



Ralph A. Clark (third from left), vice president of J. T. Baker Chemical Co., just elected chairman of the DCAT Section, confers with other new officers. In the usual order, they are William W. Huisking, of Charles L. Huisking & Co., the vice chairman; James Day, of the Dow Chemical Co., treasurer; and William J. Quinn, of Merck & Co., counsel.

Lewis Glaser Launches Lavender Sachet Business



Lewis Glaser, Charlottesville, Va., who has won fame for his quill pen industry, has launched a lavender sachet business featuring imported English lavender in dainty porous fabric containers. Each retails at 59 cents or two for one dollar.

New Suspending and Thickening Agent for Use in Cosmetics

A new chemical in the form of a fluffy, white powder, named Carbopol, which is said to have marked thickening, suspending, dispersing and emulsifying properties was demonstrated by the B. F. Goodrich Chemical Co. of Calvert City, Ky. at the Waldorf-Astoria hotel, New York City October 9.

It is a water soluble polymer and according to the manufacturer helps to make toothpaste and other cosmetics where it is applicable, smoother, eliminate the drying and caking often found in creams and lotions and help the flow of paste or liquids from plastic bottles and tubes. It is stated to be non-toxic and relatively unaffected by temperature and aging. The use of Carbopol, the company points out, may make the familiar "Shake well before using" on labels disappear from many bottled products. The use of the new product in foods is being studied. Goodrich Chemical Co., Akron, Ohio.

Fragrance Foundation Annual Meeting October 21

The annual convention of the Fragronce Foundation will be held in the Waldorf-Astoria hotel, New York, October 21. Joseph A. Danilek, president of Mary Chess Inc. and of Schaparelli Inc. is the convention chairman. Following a business meeting for members, a cocktail reception will be held at noon followed by an open meeting at which authorities will discuss topics of interest to the fragrance industry. Reservations may be

made through the Fragrance Foundation, 150 E. 42 St., New York 17, N.Y.

E. R. Durrer Reports Business Active Abroad



F. R. Durrer

E. R. Durrer, president of The Givaudan Corp. and its associate companies, has returned from an extended European trip during which he visited the Givaudan plants in Switzerland, France and England. Commenting on the economic conditions existing in the countries he visited, Mr. Durrer said that the recession experienced in the United States had no disturbing repercussions in Europe and business abroad appeared to maintain a high level of activity.



STATEMENT REQUIRED BY THE ACT OF AUGUST 24, 1912, as amended by the acts of March 3, 1933, and July 2, 1946 (Title 39, United States Code, Section 233) showing the ownership, management, and circulation of AMERICAN PERFUMER AND AROMATICS, published monthly at Bristol, Conn. for October 1, 1958.

 The names and addresses of the publisher, editor, managing editor, and business managers are: Publisher, James H. Moore, Jr., 48 West 38th St., New York 18, N. Y. Editor, William Lambert, 48 West 38th St., New York 18, N. Y. Managing editor, None. Business manager, John H. Muller, 48 West 38th St., New York 18, N. Y.

2. The owner is: (If owned by a corporation, its name and address must be stated and also immediately thereunder the names and addresses of stockholders owning or holding 1 percent or more of total amount of stock. If not owned by a corporation, the names and addresses of the individual owners must be given. If owned by a partnership or other unincorporated firm, its name and address, as well as that of each individual member, must be given.) Moore Publishing Co., Inc., 48 West 38th St., New York 18, N. Y.; J. H. Moore, 48 West 38th St., New York 18, N. Y.; Gertrude A. Moore, Indian Head Point Road, Riverside, Conn.; H. O. Andrew, 48 West 38th Street, New York 18, N. Y.

 The known bondholders, mortgagees, and other security holders owning or holding 1 percent or more of total amount of bonds, mortgages, or other securities are: (If there are none, so state.) None.

4. Paragraphs 2 and 3 include, in cases where the stockholder or security holder appears on the books of the company as trustee or in any other fiduciary relation, the name of the person or corporation for whom such trustee is acting; also the statements in the two paragraphs show the affiant's full knowledge and belief as to the circumstances and conditions under which stockholders and security holders who do not appear upon the books of the company as trustees, hold stock and securities in a capacity other than that of a bona fide owner.

5. The average number of copies of each issue of this publication sold or distributed, through the mails or otherwise, to paid subscribers during the 12 months preceding the date shown above was: (This information is required from daily, weekly, semiweekly, and triweekly newspapers only.)

James H. Moore, Jr. (Signature of publisher)

Sworn to and subscribed before me this 18th day of September, 1958.

[SEAL] MORRIS HOCHBER

(My commission expires March 30, 1959)

Parfums de Corday Premieres Perfume TRAPEZE in Montreal

Parfums de Corday of Paris and New York was host on the flagship "Flying Trapeze" September 30, to a planeload of top representatives, 60 strong, for a debut of the company's new French perfume Trapeze at Montreal's Ritz Carlton Hotel.

The group, headed by Benson Storfer, president of Parfums de Corday, was transported directly to the Ritz Carlton's Blue Room for a dinner and a special program of entertainment culminating in the presentation of Trapeze.

Elmer Bobst Outlines Opportunities for Pharmacists in Industry

Elmer H. Bobst, chairman of the board of Warner-Lambert Pharmaceutical Co. was the speaker at the first Fall meeting of the Society of Pharmacists in Industry at the Academy of Science, New York, October 9. A large and appreciative audience listened attentively as he spoke on "Opportunities for Pharmacists in Industry."

Beginning as a drug clerk in Philadelphia Mr. Bobst launched on an interesting and highly successful career, culminating with his present position as chairman of the board of Warner-Lambert Pharmaceutical Co.

Bonne Bell Cites Teen-Age Market

In her luncheon talk given to the "Cosmetic Career Women" at the Waldorf on September 30, Bonne Bell, vice-president of the company that bears her name, won her audience by her human, personal approach to her subject of the teen-ager as a cosmetic customer. Her first program for a high school group was so well received that this was the beginning of an extensive Bonne Bell teen-age program. Bonne admits:

"To me, it is the most gratifying work I've been asked to do since I joined the company. These youngsters are so eager to learn all they can about fashion and beauty. I learned quickly never to sell these teens short. They do have money and they are eager to part with it if they are treated like adults by the sales people. There are over 8 million teen-age girls and they have over 4½ billion dollars to spend. The teen-age girl puts 17% of the money she receives or earns each weeks into cosmetics."

Bonne points out that the teen-age customer needs the help of trained and sympathetic salesgirls, ones who are interested in her as a person, informed about her problems. With teen-agers, personal service means everything. Self-service can't do the job. With millions of dollars being spent to influence the school-ager, we must make sure that our sales people know how to encourage this profitable market. As Bonne says, "It takes a rather stout-hearted girl to walk up to a glittering cosmetic counter and ask, "What lipstick color would be best for me', when the average salesgirl is wearing a 'don't touch the merchandise' look."

TRAPEZE Makes Flying Debut



"Mademoiselle Trapeze"—shown at Idlewild Airport with Benson Storfer, President of Parfums de Corday, and the new "Trapeze," just before takeoff for a 60-strang press gala in Montreal to launch this Paris-born scent in the New World.



Committee for Cosmetic Career Women's Luncheon Starting its Fifth Year: left to right: Mimi Bailiff, Henrietta Meredith, Bonne Bell, guest speaker, Carolyn Hyde, Neva Bradley, program chairman, and Carolyn Jackson.

"The salesgirl should give both sincere and honest advice," says Miss Bell. "Basic needs such as a good cleanser, a medicated lotion or masque for a problem skin, a light natural make-up are what should be sold along with 'how to' help. Salesgirls can do a great deal to

build up a teen-age following through keeping mailing lists and notifying these customers of special events of interest. Addressing groups such as Y-Teens, Home Economics Classes, and Girl Scouts is also a wonderful means of developing this market."

Hazel Bishop Inc. Appoints Three District Sales Managers

As a part of a revitalization program Robert Urban, president of Hazel Bishop Inc. announces the appointment of three new district sales managers. John M. Dunnett Jr. has been named sales manager of the Eastern division; John Mc-Kenzie Jr. sales manager of the Southwest division and Leonard J. Bertoli Jr. sales manager of the Central division.

American Cholesterol Products Appoints Sales Representative

The American Cholesterol Products, Inc. of Amerchol Park, Edison, N. J., has announced the appointment of Whittaker, Clark & Daniels, Inc. of 260 West Broadway, New York City, as its export sales representative.

American Cholesterol Products, Inc. manufactures sterol and lanolin derivatives which are widely used in all types of cosmetic and pharmaceutical preparations. Whittaker, Clark & Daniels, Inc. supplies basic materials for the cosmetic, toilet goods and pharmaceutical industries, employing agents the world over to handle sales inquiries and render technical asistance when necessary.

Officials of both companies are confident that the convenience of on-the-spot representation will ease language, monetary and transportation problems, and lead to greatly increased use of the already well known "Amerchol" products in foreign markets.

OBITUARY

William R. House

William R. House, manager of the Rochester, N. Y., sales branch of the Glass Container Division of Owens-Illinois since 1947 and a veteran of 35 years with the company, died Sept. 7.

Edward J. Bork

Edward J. Bork, 55, superintendent of the Wildroot Manufacturing Corp., Buffalo, N. Y., died September 13. He joined the company at the age of 15 was promoted to superintendent in 1952.

Russell H. Young

Russell H. Young president of the Davies-Young Soap Co., Dayton, Ohio died September 20 at the age of 58 years. He was a member of the board of governors of the Chemical Specialties Manufacturers Assn. and a director of the Assn. of American Soap & Glycerine Producers.

Charles D. Allen

Charles Doughty Allen, 79, retired vice-president of H. Kohnstamm & Co., Inc., chemical firm, died at his summer home in Sagamore Beach, Mass. on September 7. A former resident of Garden City, L.I., he lived in Champlin Square, Essex, Conn.

He was associated with the Kohnstamm firm for more than fifty years, retiring in 1954 for reasons of health. Mr. Allen was a member of the American Institute of Chemical Engineers and had served with the vestry of the Protestant Episcopal Cathedral of the Incarnation of Garden City.

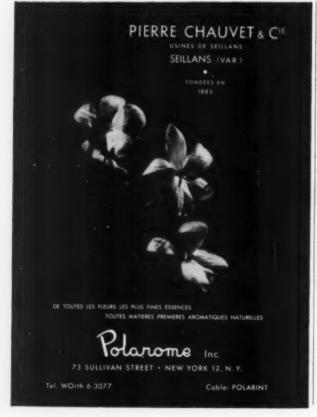
Surviving are his wife, Mrs. Lila Hammett Allen, a son, Lt. Cmdr. Charles D. Allen, Jr., and two daughters, Mrs. William S. Bliss and Mrs. Dewey F. Fagerburg, Jr.

Harry T. Johnson

Harry T. Johnson, retired cosmetic executive, was in the toilet goods industry for almost forty years, during which time he held top executive positions as vice president and general manager of famous cosmetic houses—Elizabeth Arden, Helena Rubinstein, Frances Denney, Corday.

His career goes back to the 1921 pioneering days in the treatment and cosmetic industry when he started with the famous cosmetic house of Vivaudou. In 1925 he was District Sales Manager of the original Park & Tilford Cosmetic House. He was one of the foremost authorities on merchandising, packaging and sales promotion. His work was so outstanding that both Helena Rubinstein and Elizabeth Arden hired him at record high salaries.

Harry T. Johnson was born in Montreal, Canada, and died in Garden City, Long Island, September 23, 1958. He is survived by his wife Illis Johnson, two daughters, Mrs. John D. Baxley and Alice Helene Johnson, and one son, Russell H. Johnson.





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The first children's liquid multivitamin in an aerosol container has been launched by Abbott Laboratories, North Chicago, Ill. The product is a lemon candy-flavored vitamin formula named Vi-Daylin and is an homogenized mixture of vitamins A, D, B₁, B₂, B₆, B₁₂, C and nicotonamide.

A new "Gift for Two" consisting of an attractive, compact package containing a bottle of Shalimar cologne for a woman and a bottle of extra dry cologne for a man, has been launched by Guerlain Inc. The matching square bottles contain three ounces each and the package retails for \$8. It is intended for gift purposes.

Medicated shampoos are gaining favor with women according to a survey by the Home Makers Guild of America for the Owens-Illinois Glass Co. It revealed that 13.3% of the hundreds of women interviewed are using a medicated shampoo compared with 9.5% a year ago. These data were also found: 29.8% use medicated shampoo every time they wash their hair: 31.7% use it part of the time; and 38.5% use it only when necessary.

The beaviest Christmas advertising campaign in its history has been scheduled by Shulton Inc., New York, N. Y. to promote its gift items of Old Spice for men and women's toiletries. All types of media are to be used.

The right of a manufacturer to refuse to sell to retailers who do not maintain suggested minimum prices will come before the U. S. Supreme Court on an appeal by the Justice Dept. The government is seeking to upset a lower court ruling upholding the policy of Parke Davis & Co. to refuse to sell to price cutters in Virginia and in the District of Columbia.

Variety store volume of sales of cosmetics and drugs in 1957 increased over the year before according to a report of the Harvard Business School. This was the first time that had been done since 1940.

What's New in Chemistry is the theme of the 30th annual symposium of the Assn. of Consulting Chemists and Chemical Engineers to be held in the Biltmore hotel, New York City, October 28, at 3 p. m.

The 141st class to enter the Philadelphia College of Pharmacy and Science was welcomed by President Ivor Griffith at a special convocation, September 19. Regular classes for over 200 entering students began September 29.

Plough Inc., Memphis, Tenn. manufacturer of cosmetics and pharmaceuticals has purchased the capital stock of the Creolin Co. makers of disinfectants from Merck & Co. and William Pearson Ltd. of London, England. Manufacturing and sales rights for Creolin a household disinfectant and two veterinary disinfectants are included in the sale.

A new 50-million-pounds-per-year of fluorocarbon propellants unit of Union Carbide Chemicals Co. in Institute, W. Va. is to be in operation this Autumn.

Nestle-LeMur Co. has acquired its third company in the pharmaceutical field by the purchase for cash of 80% of the stock of the E. L. Patch Co.

Highest sales in the history of Lehn & Fink Products Corp., New York, N. Y. were reported for the fiscal year ended June 30. Sales were \$30,464,197 and earnings after taxes were \$1,080,134.

For the customer who needs production help fast on special organic chemicals a new semi-commercial plant has been placed in operation by the Dow Chemical Co. Midland, Mich. The \$500,000 plant is to provide another means of bridging the time gap between the laboratory bench and full scale production.

The Glass Container Manufacturers Institute will hold its semi-annual meeting at the Cloisters, Sea Island, Georgia, November 10-13.

Purchasing agents who buy chemicals will tell "What Sells Me" at the annual sales clinic of the Salesmen's Assn. of the American Chemical Industry at the Hotel Roosevelt, New York City, October 20. Four papers are scheduled for the morning session and two panel sessions in the afternoon. The theme of the first will be "What Sells Me" and the second "What is Effective Selling?" Numerous authorities will make up the panels.

A selected audience of over 700 attended the sixteenth annual presentation of the 1958 awards honoring excellence in the field of fashion design sponsored by Coty, Inc. The presentations were made in the Metropolitan Museum of Art October 1.

The first meeting of the American Society of Perfumers was held September 17. As it was a meeting for members only the session was taken up with the president's report and committee chairmen reports followed by a discussion of old and new business.





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PERSONALITIES

Maurice Cola, Roure Bertrand Fils & Justin Dupont, Paris France, accompanied by Mrs. Cola have returned home William H. Dunney, Jr., director of the perfume laboratories and vice president of Ungerer & Co., accompanied by Mrs. Charles R. Ruston has been appointed to the national marketing committee staff of Max Factor & Co. He was formerly



Maurice Colo

after a business-pleasure trip to Mexico, Guatemala and Canada. The entire trip was made by airplane and took about three months. Before leaving New York for France Mr. Cola visited friends in the trade and conferred with executives of Roure-Dupont Inc. New York. Mr. Cola reported that business was generally good in Mexico and in Central America.

Gene D. Wilken joined the executive staff of Yardley of London in the newly created position of director of marketing, according to a recent announcement by John F. Bales, vice president in charge of sales. Mr. Wilken will participate



William H. Dunney, Jr.

Dunney, recently returned from a month's survey and pleasure trip to the principal countries of Europe. Mr. Dunney drove through the territories of Grasse, St. Simeon, Cannes, Nice, and the French Alps, where he took many pictures. During his stay in Paris, Mr. Dunney spent considerable time with Rene Bernard, manager of the French office of Ungerer-Vidal Charvet, a U.S. owned subsidiary of Ungerer & Co., New York.

Dr. Joseph Migliarese has been appointed head of Colgate-Palmolive Co.'s new laboratory for biological research



Charles R. Ruston

vice president in charge of sales for Revlon Inc. and prior to that was with the Colgate-Palmolive Co.

Col. Joseph Baird Magnus, Magnus Mabee & Reynard Inc. executive, received a special citation October 7 from the National Military Order of World Wars. The presentation was made at the Seven Regiment Armory, New York City and marked the second time it had been awarded to a non-member of the organization. Col. Magnus is commandant of the Veterans Corps of Artillery of New York State. The first was ex President Herbert Hoover.



Gene D. Wilken

with top management in the establishment of policies and objectives and will be responsible for co-ordinating the functions of the sales, merchandising, and advertising departments.

Justus H. Knam has been appointed sales engineer for Connecticut and lower New York by the L. A. Whitney Co., Needham, Mass., a packaging-systems engineering and sales service.



Dr. Joseph Migliarese

located adjacant to Rutgers University, New Brunswick, N. J. He was formerly on the Rutgers University Staff.

Hon. Rudolph F. King, former speaker of the Massachusetts House of Representatives and a former trustee of the New England College of Pharmacy took over new duties as director of development for the college September 1.



Fred W. Webster

Fred W. Webster, vice president of van Ameringen-Haebler, Inc., is serving as chairman of the Cosmetics and Toilet Goods Division in the current Sister Elizabeth Kenny Foundation fund drive.

Arthur S. Posner has resigned as president of the Paragon Distributing Corp. which distributes Roux and Eternol hair preparations.

E. J. Rhein, widely known in the scientific glassware business has retired

Joseph A. Ungerland has been appointed to the office of vice president of Lucien LeBozec has taken over the management of the cosmetic department



E. J. Rhein

after 28 years with the Kimble Glass Co., a subsidiary of the Owens-Illinois Glass Co. He joined Kimble as assistant sales manager in 1930 and became manager of the sicentific division in 1939 until he became a consultant for the division June 1 of this year.

H. Gregory Thomas, president of Chanel, Inc., has agreed to serve as chairman of the Cosmetics Division for the \$1,000,000 campaign of the New York Arthritis and Rheumatism Foundation, according to a recent announcement by E. D. Bransome, campaign chairman.



Joseph A. Ungerland

Polak & Schwarz, Inc. Mr. Ungerland has been with the organization for the past eighteen years and has been active in the industry since 1933.

Kenneth White formerly vice president in charge of sales for the Bon Ami Co. has been appointed product manager on the Halo shampoo and men's lines of the toilet articles division of the Colgate-Palmolive Co.

Robert J. Gillen Jr. has been appointed coordinator of advertising and merchandising for Hazel Bishop, Inc., New York.



Lucien LeBozec

of Kong Hermanos, in Guatemala City, Guatemala, C. A., and has made commendable progress in developing the cosmetic business throughout the country. Mr. LeBozec founded Parfumerie Richemond in Paris, France for which he also served as chemist and perfumer, before assuming his present position.

Ralph S. Harte has been appointed vice president of Goubaud de Paris Inc., New York and will be in charge of the wholesale division. Before joining Goubaud de Paris Mr. Harte was the founder of his own firm, Harte & Co., a plastic manufacturing concern.

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Sales Volume Up

S eptember sales of essential oils and aromatic chemicals increased in volume. General improvement in the economy and a hardening price trend spurred interest in an extended line of items with the inquiry indicating a more pronounced upturn in October. A portion of the upturn in September was

attributed to preparations on the part of perfumers and toiletry manufacturers for the coming year end holidays although consumer inventories which had been allowed to run down to a low point during the summer vacation period also played a part in the upturn.

TRENDS IN DETAIL

Advances	Current	Previous
Alcohol, tankears, gal.		
Ethyl, 190 proof	\$ 0.52	\$ 0.47
Special denatured 40	0.56	0.48
Proprietary solvent	0.56	0.50
Isopropyl, 99%	0.46	0.41
Oil spearmint	5.75	4.75
Oil petitgrain	2.40	2.25
Copra, coast, ton	195.00	192.50
Oil geranium		
Bourbon	19.50	17.00
Algerian	16.75	15.75
Oil celery	13.50	13.00
Oil amyris	1.25	1.10
Declines		
Oil cananga		
Native	6.50	7.00
Rectified	8.50	8.85
Oleo resin ginger	10.00	14.00
Oil cintronella, Formosan	0.58	0.63
Oil orange		
Californian, coldpressed	2.35	3.35
Californian, distilled	0.90	1.25
Floridian	1.80	2.10
Oil peppermint, natural	4.15	4.50
Tallow, fancy	0.08	0.083/8
Vanilla beans, Bourbon	10.50	11.00

ALCOHOL PRICES ADVANCE-

Prices on isopropyl and ethyl alcohol were boosted five to eight cents a gallon October 1 to reflect mounting labor, denaturant, and other costs. It was the first change in the market in two years. The advances in isopropyl alcohol amounted to five cents a gallon. With the exception of specially denatured 40 and proprietary solvent alcohol which rose eight cents and six cents, respectively, all denatured grades were moved up five cents a gallon. The advance in ethyl alcohol brings the price in tankcars to 52 cents a gallon in contrast to 47¢ previously in effect.

RHODINOL ADVANCING-

The trend in rhodinol continues upward. Seasonal influences are creating a greater demand for the material. Rising costs of geranium oil threaten to force rhodinol prices to higher levels. Latest rise brought selling prices up to \$43 to \$46 per pound in 25-pound cans depending on quality.

ORANGE LOSING GROUND-

In addition to a sharp break in Californian orange oil prices amounting to about 30 percent, the trend in Floridian orange has been steadily downward with the latter article falling to \$1.80 per pound. With the most active consuming season in beverages having come to a close greater selling prevails. The freeze that hit the Florida crop in the early months of this year brought a rush of orders for the oil, and it is reported that buyers have not been able to work off as much of their inventories during the summer months as they had expected. The coming crop in December is likewise serving to create greater selling pressure in the market.

SPEARMINT OUTLOOK STRONG-

With confectioners reported having purchased a good portion of this year's production of spearmint oil the outlook is generally regarded as strong. A series of advances accompanied the heavy demand. A smaller output this year is also a contributing factor to the firmness in prices.

MENTHOL CONSUMPTION RISING-

Consumption of menthol is rising particularly in the tobacco and toiletry trades. The supply position continues long however with the tone of the market remaining highly unsettled in the view of good stocks of the natural product from Brazil hanging over the local market. The first actual synthetic replacement is expected for laevo menthol which heretofore has been made solely from imported natural oils. Plans for the construction of a \$2 million chemical plant to produce the new product have been announced. The basic material that will be used will be a pine product.

PEPPERMINT OIL SOFTENS-

Influenced by lower prices from the Farwest prices on peppermint oil lost ground over the past month. Prices out of the Midwest remained quite firm, however, particularly for high test oil. Some trade observers are inclined to take a firm view regarding the long term outlook.

LARGE GLYCERIN ARRIVALS EXPECTED-

Crude glycerin imports are expected to be heavier in the last half of this year than in the first six months. Substantial tonnages expected to arrive this month. The arrivals will come from various parts of the world including Indonesia, India, Japan and other countries. The material will serve as a supplement to domestic crude which has remained in a very tight supply position for many months. Prices on refined glycerin remain steady and are expected to remain at current levels over the remainder of the year.

STYRAX GUM REMAINS SCARCE-

The acute shortage of Asiatic styrax has failed to be relieved and prices on the Honduran variety have been slowly edging upward. Latest change in Honduran styrax was an increase of 25 cents per pound to a level \$3.75 to \$4.

OIL ROSEWOOD SOFT-

While the downward trend in rosewood oil appears to have been slowed, the market remains in a competitive position. Prices on Peruvian material continue to be subject to shading in view of good stocks and a narrow demand.

VANILLA BEANS QUIETER-

High prices have tended to dampen trade in vanilla beans. Most dealers are asking \$11 per pound for Bourbon beans but occasional lots are reported available at \$10.50 to \$10.75. The market in Madagascar is somewhat different than at this time a year ago. Virtually no sales of new crop beans have been made for January forward shipment. At this time last year 50 percent of the crop had been sold.

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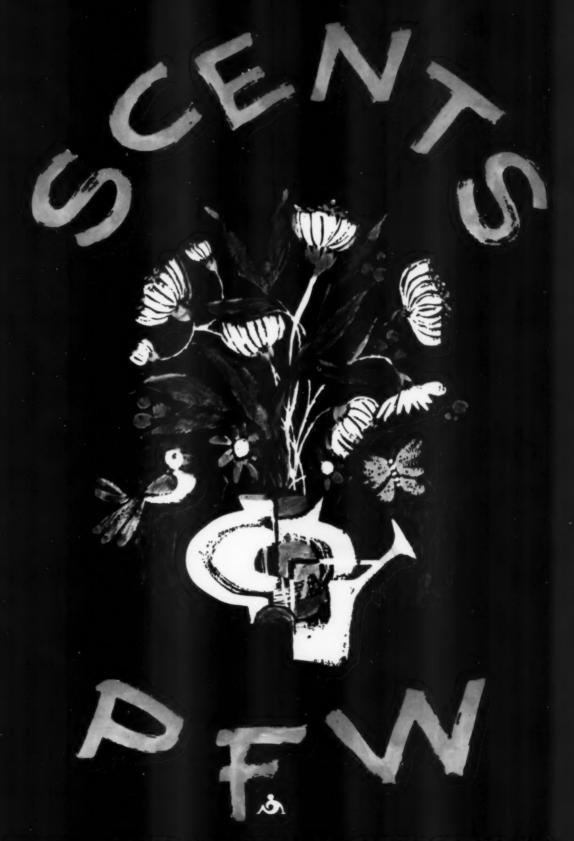
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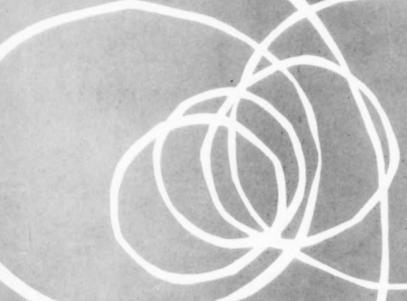
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